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Entropy Stable Discretization of Compressible Flows in Thermochemical Nonequilibrium

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ABSTRACT

Entropy stable numerical methods for compressible flow have been demonstrated to exhibit better robustness than purely linearly stable methods and need less overall artificial dissipation for long simulations in subsonic and transonic flows. In this work we seek to extend these benefits to multicomponent, multitemperature flows in thermochemical nonequilibrium such as combustion and hypersonic flight. We first derive entropy functions that symmetrize the governing equations and allow stability proofs for such systems. The impact of diffusion model selection on provable entropy stability is considered in detail, including both rigorous models of irreversible thermodynamics and simplified models of greater practical interest. Based on the proven entropy functions we develop affordable, entropy conservative two-point flux functions for solution in conservation form. We derive entropy conservative fluxes for calorically and thermally perfect mixtures, with heat capacities described by either polynomials of the temperature or formulas from statistical thermodynamics.

CONTENTS

1. INTRODUCTION

Entropy stability and summation-by-parts (SBP) operators provide a rigorous foundation for the development of provably-stable, high-order, and conservative methods for nonlinear conservation laws such as the Euler and Navier-Stokes Equations. Entropy stability provides a nonlinear integral stability estimate and constrains weak solutions to be consistent with the second law of thermodynamics. The objective of this work is the extension of entropy stability to compressible flows in thermochemical nonequilibrium. We consider both fundamental stability of the continuous equation system and the construction of semi-discrete systems that mimic stability of the continuous system.

Early studies of conservation laws with an entropic structure and corresponding symmetric form were made by Godunov [12], Mock [18], and Lax and Friedrichs [11]. Harten [13] derived a family of entropy functions of the Euler equations. Hughes et al. [15] demonstrated symmetrization of the Navier-Stokes equations with heat conduction. The inclusion of heat conduction limited the family of admissible entropy functions to only those trivially different than the thermodynamic entropy. Chalot et al. [5] extend symmetrization from the Navier-Stokes equations [15] to the multicomponent systems in thermochemical nonequilibrium, assuming a two-temperature model. Both of Hughes et al. [15] and Chalot et al. [5] cast equations in symmetric form for numerical solution with a Galerkin finite element method (FEM) so that the discretized system inherits the stability properties from the continuous system. Rotation to symmetric form, however, destroys consistency with the Lax-Wendroff theorem.

To attain discrete entropy stability and consistency with the Lax-Wendroff theorem, Tadmor [22] designed second-order finite-volume methods, identifying an entropy conservation condition for two-point flux functions. LeFloch et al. [17] develop the extension to fully-discrete, higher-order methods on periodic domains. Computational tractability is addressed by the 'affordable' entropy stable flux functions of Roe and Ismail [16] and later extended by Winters and Gassner [26] to magnetohydrodynamics. Fisher and Carpenter [9] show that entropy stability is possible for any spatial discretization that can be expressed with diagonal norm SBP operators. It is shown that entropy stable high-order fluxes may be calculated from two-point flux functions satisfying the condition of Tadmor [22].

In this manuscript we derive an entropy function to symmetrize compressible flow equations in thermochemical nonequilibrium system, applicable to multicomponent and one-, two-, and three-temperature models. Based on this entropy function we further develop an affordable, entropy conservative inviscid flux function for multicomponent, compressible, and single or multitemperature flows in conservation form, a key distinction between this work and that of Chalot et al. [5], which focuses on the non-conservative symmetric form for FEM solution. Additionally we discuss the impact of diffusion model selection on symmetrization and entropy stability, with a general formulation from irreversible thermodynamics and simplified models of practical interest.

This manuscript can be broken into four parts.

1. In Section 2 we first discuss relevant background information regarding entropy stability of general advection-diffusion-reaction problems (§2.1) and analogous semi-discrete problems built with SBP operators (§2.2).
2. Section 3 details the governing equations and constitutive relations for compressible, multicomponent, multitemperature systems relevant to combustion and hypersonic flight.

3. In Section 4 we derive entropy functions and demonstrate entropy stability for a variety of systems in thermochemical nonequilibrium, beginning with a derivation of thermodynamic entropies in §4.1. Then single-temperature systems are considered first in §4.2, where we develop entropy functions for multicomponent and either calorically or thermally perfect mixtures along with conditions on diffusive flux models. We extend the entropy stability proofs to three-temperature mixtures in §4.3.
4. Having shown entropy stability of the continuous systems, in Section 5 we derive entropy conservative two-point flux functions in conservation form for single-temperature (§5.2) and multitemperature (§5.3) systems. We discuss in §5.1 an automated method of deriving two-point flux functions satisfying Tadmor's condition [22] and generalize the idea of the logarithmic average of Roe and Ismail [16] as will be necessary to develop fluxes for thermally perfect gases.

2. ENTROPY STABILITY BACKGROUND

2.1. Continuous Advection-Diffusion-Reaction Problems

In differential form the governing equations for a multicomponent (n_c components), multitemperature (n_t temperatures), compressible, viscous gas on the interior of an n_d-dimensional domain Ω with bounding surface Γ in coordinates $\{x_i\}$ are

$$\boldsymbol{q}_t + \boldsymbol{f}^{x_i}_{x_i} - \boldsymbol{f}^{v,x_i}_{x_i} - \boldsymbol{r} = \boldsymbol{0}, \tag{1}$$

where $\boldsymbol{q}(\boldsymbol{x}, t) \in \mathbb{Q} := (\mathbb{R}^+)^{n_c} \times \mathbb{R}^{n_d} \times (\mathbb{R}^+)^{n_t}$ is the mapping from time t and spatial coordinates $x_i \in \Omega$ to the $n_v = n_c + n_t + n_d$ conserved state variables, $\boldsymbol{f}^{x_i}, \boldsymbol{f}^{v,x_i} \colon \mathbb{Q} \to \mathbb{R}^{n_v}$, $i = 1, \ldots, n_d$, are the inviscid and viscous fluxes in the x_i direction, respectively, $\boldsymbol{r} \colon \mathbb{Q} \to \mathbb{R}^{n_v}$ is the source term of chemical reaction and thermal excitation rates, the subscripts indicate partial differentiation, and Einstein notation is used to imply summation over repeated indices. Physical details of the governing equations for systems of interest are given later in §3. Until then (1) is considered as a general system of nonlinear advection-diffusion-reaction equations.

An important challenge in mathematics and computing is determining the stability of (1) and its discretized forms. This is a practical matter in computing, where *ad hoc* techniques such as hyper-viscosity and filtering for improved stability can degrade accuracy and break down due to their disconnection from rigorous mathematics. Linear analyses have proven to be useful in developing stable numerical methods but nonlinear problems with discontinuities such as shocks require a nonlinear analysis. Central to the technique of nonlinear entropy stability analysis is the entropy function and fluxes, defined in Definition 2.1.

Definition 2.1. An entropy function of (1) is a convex scalar function $\mathcal{S} \colon \mathbb{Q} \to \mathbb{R}$ with corresponding entropy fluxes, $\mathcal{F}^{x_i} \colon \mathbb{Q} \to \mathbb{R}$, $i = 1, \ldots, n_d$ that satisfy the compatibility relation $\mathcal{S}_{\boldsymbol{q}} \boldsymbol{f}^{x_i}_{x_i} = \mathcal{F}^{x_i}_{x_i}$, if the governing equations written with the entropy variables $\boldsymbol{w}^\top := \mathcal{S}_{\boldsymbol{q}}$,

$$\boldsymbol{q}_{\boldsymbol{w}} \boldsymbol{w}_t + \boldsymbol{f}^{x_i}_{\boldsymbol{w}} \boldsymbol{w}_{x_i} - \left(\hat{\mathrm{C}}_{i,j} \boldsymbol{w}_{x_j}\right)_{x_i} - \boldsymbol{r} = \boldsymbol{0}, \tag{2}$$

satisfy the following conditions:

- The Hessian matrix, $\mathcal{S}_{\boldsymbol{qq}} = \boldsymbol{w}_{\boldsymbol{q}}$, is symmetric positive definite (a one-to-one mapping exists between the entropy variables $\boldsymbol{w}$ and conserved variables $\boldsymbol{q}$).
- The inviscid flux Jacobian matrices, $\boldsymbol{f}^{x_i}_{\boldsymbol{w}}$, $i = 1, ..., n_d$, are symmetric.
- The viscous flux coefficient matrices, $\hat{\mathrm{C}}_{i,j}$ produce a symmetric positive semi-definite matrix,

$$\begin{bmatrix} \hat{\mathrm{C}}_{1,1} & \cdots & \hat{\mathrm{C}}_{1,n_d} \\ \vdots & \ddots & \vdots \\ \hat{\mathrm{C}}_{n_d,1} & \cdots & \hat{\mathrm{C}}_{n_d,n_d} \end{bmatrix} \tag{3}$$

- The entropy source term, $\mathcal{R} = \boldsymbol{w}^\mathsf{T}\boldsymbol{r}$, is negative semi-definite.

We now demonstrate the continuous stability estimate associated with an entropy function as defined in Definition 2.1. Contracting Equation (1) with the entropy variables, $\boldsymbol{w}$, yields the following evolution equation for the entropy function.

$$\mathcal{S}_t + \mathcal{F}^{x_i}_{x_i} - \boldsymbol{w}^\mathsf{T}\left(\hat{\mathrm{C}}_{i,j}\boldsymbol{w}_{x_j}\right)_{x_i} - \mathcal{R} = \mathbf{0}. \tag{4}$$

Integrating over the domain and utilizing integration by parts for the viscous term yields the time rate of change of the total entropy in the domain:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \mathcal{S}\mathrm{d}V = \int_\Gamma \left(\boldsymbol{w}^\mathsf{T}\boldsymbol{f}^{v,x_i} - \mathcal{F}^{x_i}\right)\mathrm{d}S_i - \int_\Omega \boldsymbol{w}^\mathsf{T}_{x_i}\hat{\mathrm{C}}_{i,j}\boldsymbol{w}_{x_j}\mathrm{d}V + \int_\Omega \mathcal{R}\mathrm{d}V. \tag{5}$$

This equation shows that the total entropy in the domain changes due to boundary fluxes, viscous dissipation, and the source terms such as chemical reactions or thermal excitation. The positive semi-definiteness of the viscous flux Jacobian matrices means that the viscous term always dissipates entropy, as

$$\int_\Omega \boldsymbol{w}^\mathsf{T}_{x_i}\hat{\mathrm{C}}_{i,j}\boldsymbol{w}_{x_j}\mathrm{d}V = \int_\Omega \begin{bmatrix} \boldsymbol{w}_{x_1} \\ \vdots \\ \boldsymbol{w}_{x_{n_d}} \end{bmatrix}^\mathsf{T} \begin{bmatrix} \hat{\mathrm{C}}_{1,1} & \cdots & \hat{\mathrm{C}}_{1,n_d} \\ \vdots & \ddots & \vdots \\ \hat{\mathrm{C}}_{n_d,1} & \cdots & \hat{\mathrm{C}}_{n_d,n_d} \end{bmatrix} \begin{bmatrix} \boldsymbol{w}_{x_1} \\ \vdots \\ \boldsymbol{w}_{x_{n_d}} \end{bmatrix} \mathrm{d}V \geq 0. \tag{6}$$

The negative semi-definiteness of the entropy source term, $\mathcal{R}$, guarantees that source terms such as chemical reactions and thermal excitation dissipate entropy. Equation (5) thus bounds the growth rate of the total entropy in the domain, providing an L_2 estimate on solutions of (1) provided that $\mathcal{S}_{\boldsymbol{qq}}$ remains symmetric and positive definite for all time.

Also relevant to entropy analysis of (1) is the entropy potential, $\varphi\colon \mathbb{R}^{n_v} \to \mathbb{R}$, and the entropy potential fluxes, $\psi^{x_i}\colon \mathbb{R}^{n_v} \to \mathbb{R}, i = 1, \ldots, n_d$. These scalar functions of the entropy variables arise out of the symmetry of the Jacobian matrices $\boldsymbol{q}_{\boldsymbol{w}}$ and $\boldsymbol{f}^{x_i}_{\boldsymbol{w}}$, wherein the conserved variables and fluxes are viewed as gradients of the potential and potential fluxes with respect to the entropy variables [13]. The symmetry and positive definiteness of $\boldsymbol{q}_{\boldsymbol{w}} = \varphi_{\boldsymbol{ww}}$ shows the convexity of $\varphi(\boldsymbol{w})$. As shown by Mock [18], for the entropy function $\mathcal{S}$, entropy fluxes $\mathcal{F}^{x_i}$, and symmetrizing variables $\boldsymbol{w}$, these functions are given by

$$\varphi = \boldsymbol{q}^\mathsf{T}\boldsymbol{w} - \mathcal{S}, \tag{7}$$

$$\psi^{x_i} = (\boldsymbol{f}^{x_i})^{\mathsf{T}}\boldsymbol{w} - \mathcal{F}^{x_i}, \quad i = 1, \ldots, n_d. \tag{8}$$

The potential and potential flux are referred to as a pair, (φ, ψ^{x_i}). The entropy potential flux is particularly important in the derivation of entropy conservative semi-discrete schemes as shown by Fisher and Carpenter [9] and used in §5.

Before moving on we briefly discuss the viscous terms in (1). While Harten [13] showed the existence of a family of entropy functions for the inviscid Euler equations, Hughes et al. [15] showed that the presence of heat conduction in the Navier-Stokes equations means that only trivial functions of the thermodynamic entropy are admissible. The presence of mass diffusion is a significant complexity of the systems considered herein. Chalot et al. [5] treat species mass diffusion with the general theory of irreversible thermodynamics that guarantees consistency of the viscous fluxes with the second law of thermodynamics. This treatment of mass diffusion is not a common one due to its complexity and far simpler models such as Fick's law and mixture-averaged diffusion are often utilized instead. Having identified this difficulty, our approach is to first derive an entropy function, built atop the thermodynamic entropy, that satisfies conditions on the hyperbolic part of the system and the source terms. Given this entropy function we develop and apply a general analysis of the provable stability of models for mass and heat diffusion.

2.2. Semi-Discrete Problems

Numerical solution of (1) requires discretization of space and time. We consider spatial discretizations using summation-by-parts operators (SBP), which encompasses finite difference [10], finite element [4], and finite volume [19] methods. For SBP operators, the gradient in a given direction, α, is restricted to the form,

$$\mathcal{D}_\alpha = \mathcal{P}_\alpha^{-1}\mathcal{Q}_\alpha, \quad \mathcal{Q}_\alpha + \mathcal{Q}_\alpha^{\mathsf{T}} = \mathcal{B}_\alpha, \tag{9}$$

subject to accuracy constraints, diagonal mass matrix $\mathcal{P}$, and $\mathcal{B} = \mathcal{B}^{\mathsf{T}}$ is an accurate boundary integral operator. We use Greek subscripts to indicate no summation over repeated indices. See del Rey Fernandez, et al. [8] for a detailed review of SBP operators. A possible linearly-stable semi-discretization of (1) would be

$$\mathsf{q}_t + \mathcal{D}_k\left(\mathsf{f}^{x_k}(\mathsf{q}) - \mathrm{C}_{kj}\mathcal{D}_j\mathsf{q}\right) - \mathsf{r}(\mathsf{q}) - \mathsf{g}_b = 0, \tag{10}$$

where g_b enforces boundary conditions through the simultaneous approximation terms (SAT) and q indicates the discrete solution of (1). However, this is inadequate for stability in simulating underresolved flows and flows that admit shocks. Following recent developments in entropy stable methods for the perfect gas equations [9], we discretize (1) with

$$\mathsf{q}_t + \left[2\mathcal{D}_k \circ \mathcal{F}_k^S\right]\mathsf{1} - \mathcal{D}_k\mathrm{C}_{kj}\mathcal{D}_j\mathsf{w}(\mathsf{q}) - \mathsf{r}(\mathsf{q}) - \mathsf{g}_b = 0. \tag{11}$$

The new nonlinear advective operator (equivalent to a Hadamard product, $\circ$ and a new flux coefficient matrix) is defined using

$$\left[2\mathcal{D}_k \circ \mathcal{F}_k^S\right]_{\beta\gamma} = 2d_{k\beta\gamma}\boldsymbol{f}^{S,k}(\boldsymbol{q}_\beta, \boldsymbol{q}_\gamma), \tag{12}$$

where d_{kij} corresponds to row i and column j of $\mathcal{D}_k$, and $\boldsymbol{f}^{S,k}(\boldsymbol{q}_i, \boldsymbol{q}_j)$ is an entropy conservative two-point flux function in direction k. The central missing piece to constructing entropy stable operators for flows exhibiting thermochemical nonequilibrium is that until now an affordable version of this two-point flux function has been unknown. Such fluxes must satisfy two fundamental constraints for entropy stability. First, the flux must be consistent, meaning that it is equivalent to the physically correct flux when the two states are identical,

$$\lim_{\boldsymbol{q}_\ell, \boldsymbol{q}_r \to \boldsymbol{q}} \boldsymbol{f}^{S,x_k}(\boldsymbol{q}_\ell, \boldsymbol{q}_r) = \boldsymbol{f}^{x_k}(\boldsymbol{q}). \tag{13}$$

Second, the flux must satisfy Tadmor's local condition [9, 22],

$$(\boldsymbol{f}^{S,x_k})^\mathsf{T} \Delta \boldsymbol{w} = \Delta \psi^{x_k}, \tag{14}$$

where $\Delta a = a_r - a_\ell$ is the jump and ψ^{x_k} is the entropy potential flux in direction x_k introduced in §2. Derivation of two-point fluxes that satisfy these conditions is undertaken in §5. Appropriate fluxes are given in §5.2 for multicomponent, single-temperature (thermal equilibrium) mixtures and in §5.3 for mixtures exhibiting varying degrees of thermal nonequilibrium (*e.g.*, two- and three-temperature models).

Using the discretization (11), we can show that the semi-discrete equation mimics the entropy stability of the continuous equation by contracting the governing equation against the entropy variables and integrating discretely over the volume,

$$\mathsf{w}(\mathsf{q})^\mathsf{T} \boldsymbol{\mathcal{P}} \left[\mathsf{q}_t + \left[2\mathcal{D}_k \circ \mathcal{F}_k^S\right] \mathsf{1} - \mathcal{D}_k \mathrm{C}_{kj} \mathcal{D}_j \mathsf{w}(\mathsf{q}) - \mathsf{r}(\mathsf{q}) - \mathsf{g}_b\right] = 0. \tag{15}$$

Due to the diagonal volumetric mass matrix $\boldsymbol{\mathcal{P}} = \mathcal{P}_1 \mathcal{P}_2 \mathcal{P}_3$, we can bound the integral of S_t,

$$\begin{aligned} \mathsf{1}^\mathsf{T} \boldsymbol{\mathcal{P}} \mathsf{S}_t + \mathsf{w}(\mathsf{q})^\mathsf{T} \mathcal{D}_k^\mathsf{T} \boldsymbol{\mathcal{P}} C_{kj} \mathcal{D}_j \mathsf{w}(\mathsf{q}) = &- \mathsf{1}^\mathsf{T} \left[\tilde{\mathcal{B}}_k \circ \mathcal{F}_k^S\right] \mathsf{1} + \mathsf{w}^\mathsf{T} \tilde{\mathcal{B}}_k \mathrm{C}_{kj} \mathcal{D}_j \mathsf{w}(\mathsf{q}) \\ &+ \mathsf{1}^\mathsf{T} \boldsymbol{\mathcal{P}} \mathcal{R}(\mathsf{q}) + \mathsf{w}(\mathsf{q})^\mathsf{T} \boldsymbol{\mathcal{P}} \mathsf{g}_b, \end{aligned} \tag{16}$$

where

$$\tilde{\mathcal{B}}_\alpha = \boldsymbol{\mathcal{P}} \mathcal{P}_\alpha^{-1} \mathcal{B}_\alpha. \tag{17}$$

If g_b is constructed such that

$$\mathsf{w}(\mathsf{q})^\mathsf{T} \boldsymbol{\mathcal{P}} \mathsf{g}_b - \mathsf{1}^\mathsf{T} \left[\tilde{\mathcal{B}}_k \circ \mathcal{F}_k^S\right] \mathsf{1} + \mathsf{w}^\mathsf{T} \tilde{\mathcal{B}}_k \mathrm{C}_{kj} \mathcal{D}_j \mathsf{w}(\mathsf{q}) \le \mathsf{1}^\mathsf{T} \tilde{\mathcal{B}} \mathcal{F}(\mathsf{q}_b), \tag{18}$$

where $\mathcal{F}(\mathcal{S}_b)$ only depends on boundary data, then the entropy estimate in the volume becomes

$$\mathsf{1}^\mathsf{T} \boldsymbol{\mathcal{P}} \mathsf{S}_t \le \mathsf{1}^\mathsf{T} \tilde{\mathcal{B}} \mathcal{F}(\mathsf{q}_b) - \mathsf{w}(\mathsf{q})^\mathsf{T} \mathcal{D}_k^\mathsf{T} \boldsymbol{\mathcal{P}} \mathrm{C}_{kj} \mathcal{D}_j \mathsf{w}(\mathsf{q}) + \mathsf{1}^\mathsf{T} \boldsymbol{\mathcal{P}} \mathcal{R}(\mathsf{q}). \tag{19}$$

Negative semi-definiteness of $\mathcal{R}$ implies that the entropy in the volume will be bounded by the imposed entropy flux and the scheme will be entropy stable.

Remark. We note that constructing g_b to satisfy (18) is nontrivial and beyond the scope of the current work. Our focus is on developing the two-point fluxes needed to satisfy the entropy condition in the domain interior such that entropy fluxes telescope to the boundaries in the same way as for the perfect gas equations.

3. GOVERNING EQUATIONS FOR FLOWS IN THERMOCHEMICAL NONEQUILIBRIUM

Hypersonic flight at high altitudes presents a number of opportunities and challenges for computational modeling. Flight at high speeds, high temperatures, and low density is significantly impacted by thermochemical nonequilibrium effects such as molecular dissociation and excitation of internal molecular energy modes [1]. Here we specify Equation 1 for such reacting flows that can exhibit nonequilibrium effects.

3.1. State Vectors

In perfect gas flows where thermochemical nonequilibrium effects are unnecessary, we solve $n_d + 2$ equations: one continuity equation, one for total energy conservation, and n_d linear momentum equations. By contrast for nonequilibrium flows we solve $n_v = n_d + n_c + n_t$ equations. To incorporate the effects of chemical nonequilibrium, such as molecular dissociation and recombination, n_c equations are solved for the component mass densities $\boldsymbol{\rho} \in (\mathbb{R}^+)^{n_c}$, which sum to the total density, $\rho = \mathbf{1}^\mathsf{T}\boldsymbol{\rho}$. One equation governs the total specific energy, $E \in \mathbb{R}$, and $n_t - 1$ equations govern the transport and excitation/relaxation of the modeled internal energies, which we collected into a vector $\boldsymbol{e}^* \in \mathbb{R}^{n_t-1}$. Separate equations are solved for internal energy modes that are not in equilibrium with the translational mode or other modes already modeled. For example, common two-temperature models assume that translational and rotational modes are in equilibrium at one temperature while vibrational and electronic modes are in equilibrium at another temperature. Such models involve a total energy equation and one additional equation for the total vibrational-electronic energy. A case of a three-temperature model extends this to incorporate a rotational temperature, separating translational, rotational, and vibrational-electronic modes. One may also incorporate electronic mode equations or separate vibrational-electronic temperatures per polyatomic species.

We consider multicomponent, multitemperature models without including temperatures per polyatomic species and without electron transport equations present in modeling ionized flows. The conserved state vector and 'primitive' state vector, respectively, are

$$\boldsymbol{q} = \begin{pmatrix} \boldsymbol{\rho} \\ \rho\boldsymbol{v} \\ \rho E \\ \rho\boldsymbol{e}^* \end{pmatrix}, \quad \boldsymbol{v} = \begin{pmatrix} \boldsymbol{\rho} \\ \boldsymbol{v} \\ T \\ \boldsymbol{T}^* \end{pmatrix}, \tag{20}$$

where $\boldsymbol{v} \in \mathbb{R}^{n_d}$ is the linear mass-averaged velocity vector, $T \in \mathbb{R}^+$ is the translational mode temperature and $\boldsymbol{T}^* \in (\mathbb{R}^+)^{n_t-1}$ is the vector of modeled internal mode temperatures.

3.2. Equation of State

The governing equations are supplemented by the ideal gas equation of state, which is valid for the low-density, high-temperature environments of hypersonic flight [1].

$$p = T\boldsymbol{\rho}^\mathsf{T}\boldsymbol{R}, \tag{21}$$

where $p \in \mathbb{R}^+$ is the thermodynamic pressure and $\boldsymbol{R} \in \mathbb{R}^{n_c}$ is the vector of component specific gas constants, $R_j = R_u/M_j$, based on the universal molar gas constant R_u and component molecular weight M_j.

3.3. Internal Energies

The total specific energy of the mixture, $E = e_{\text{total}} + \boldsymbol{v}^\mathsf{T}\boldsymbol{v}/2$, is the sum of total specific internal energy, e_{total}, and macroscopic kinetic energy. A number of approaches may be taken towards the computation of energy, and we consider two: the 'modal' approach (see §3.3.2) common in aerodynamics and a polynomial-based approach (see §3.3.1) common in combustion. Both of these approaches split the specific mixture energy into that of individual components and utilize a mass-weighted average to obtain the internal energy of the mixture,

$$e_{\text{total}} = \sum_{i=1}^{n_c} \rho_i e_{\text{total},i}/\rho. \tag{22}$$

3.3.1. Heat Capacity Polynomials

This approach, exemplified by the NASA polynomials [3], involves fitting polynomials in terms of the temperature for the heat capacities and enthalpies of individual species based on experimental data. Excitation of internal energy modes is incorporated in these polynomials and so the internal energy of each component is computed directly from the temperature. This approach is not valid for multitemperature regimes experienced in hypersonic flight because thermal equilibrium is assumed and a single temperature is used. We consider it here due to its utility in modeling multicomponent flows in thermal equilibrium such as combustion.

With the NASA-9 polynomials the isobaric specific heat capacity of species i is

$$c_{p,i}/R_i = a_{i,0}/T^2 + a_{i,1}/T + a_{i,2} + a_{i,3}T + a_{i,4}T^2 + a_{i,5}T^3 + a_{i,6}T^4, \tag{23}$$

and the internal enthalpy is

$$h_{\text{total},i}/R_i = a_{i,7} + -a_{i,0}/T + a_{i,1}\ln(T) + a_{i,2}T + \frac{1}{2}a_{i,3}T^2 + \frac{1}{3}a_{i,4}T^3 + \frac{1}{4}a_{i,5}T^4 + \frac{1}{5}a_{i,6}T^5, \tag{24}$$

where $a_{i,j}$ are fitting coefficients for species i. We note that the enthalpy above includes the formation enthalpy, so that the evaluation of $h_{\text{total},i}$ at the reference temperature yields the tabulated species' enthalpy of formation [3].

Based on these polynomials, the isochoric heat capacity, $c_{v,i} = c_{p,i} - R_i$, is

$$c_{v,i}/R_i = a_{i,0}/T^2 + a_{i,1}/T + (a_{i,2} - 1) + a_{i,3}T + a_{i,4}T^2 + a_{i,5}T^3 + a_{i,6}T^4, \tag{25}$$

and the internal energy, $e_{\text{total},i} = h_{\text{total},i} - R_iT$, is

$$e_{\text{total},i}/R_i = a_{i,7} + -a_{i,0}/T + a_{i,1}\ln(T) + (a_{i,2} - 1)T + \frac{1}{2}a_{i,3}T^2 + \frac{1}{3}a_{i,4}T^3 + \frac{1}{4}a_{i,5}T^4 + \frac{1}{5}a_{i,6}T^5. \tag{26}$$

3.3.2. Modal Energy Decomposition

In this approach the energy of each internal mode is calculated from formulas from statistical thermodynamics. The internal energy of a component is then simply the sum of the internal modes. When thermal nonequilibrium is modeled with multiple temperatures, the energy of each mode simply depends on a possibly unique temperature.

The translational mode, characterized by the temperature, T, has a heat capacity $c_{v,t,i}$ and energy $e_{t,i}$ of species i, respectively,

$$c_{v,t,i} = \frac{3}{2}R_i, \quad e_{v,t,i} = \int_{T^\circ}^{T} c_{v,t,i}dT = \frac{3}{2}R_i(T - T^\circ), \tag{27}$$

where T° is the reference temperature. Similarly, the rotational mode, with temperature T_r, has a heat capacity $c_{v,r,i}$ and energy $e_{r,i}$ of species i, respectively,

$$c_{v,r,i} = \nu_i R_i, \quad e_{r,i} = \nu_i R_i(T_r - T^\circ), \tag{28}$$

where ν_i is zero for monatomic species and unity for diatomic species. Note that when the rotational mode is in equilibrium with the translational mode we have $T_r = T$. The vibrational mode with temperature T_v has the following energy and heat capacity, assuming a molecular harmonic oscillator model [25],

$$e_{v,i} = \nu_i R_i \Theta_i \left(\frac{1}{\exp(\Theta_i/T_v) - 1} - \frac{1}{\exp(\Theta_i/T^\circ) - 1} \right), \tag{29}$$

$$c_{v,v,i} = \frac{\partial e_{v,i}}{\partial T_v} = \nu_i \frac{R_i \Theta_i^2 \exp(\Theta_i/T_v)}{(\exp(\Theta_i/T_v) - 1)^2 T_v^2}, \tag{30}$$

where Θ_i is the characteristic vibrational temperature. The final contribution to the internal energy considered in this work is the intrinsic chemical energy, or formation energy, $e^\circ_{f,i}$, which relates to the more commonly tabulated formation enthalpy as $e^\circ_{f,i} = h^\circ_{f,i} - R_i T^\circ$. Thus, the internal energy of species i in the modal approach, to be contrasted against (26), is

$$e_{\text{total},i} = e^\circ_{f,i} + \frac{3}{2}R_i(T - T^\circ) + \nu_i R_i(T_r - T^\circ) + \nu_i R_i \Theta_i \left(\frac{1}{\exp(\Theta_i/T_v) - 1} - \frac{1}{\exp(\Theta_i/T^\circ) - 1} \right). \tag{31}$$

In contrast to the polynomial approach, this approach may be used in multitemperature flows. We consider three versions of this model, namely one-, two-, and three-temperature models, each appropriate for different flow regimes in aerodynamics. One-temperature models have $T = T_r = T_v$, and the $\boldsymbol{e}^*$ and $\boldsymbol{T}^*$ vectors are empty. The two-temperature models considered herein have $T = T_r \neq T_v$ (translational-rotational modes at temperature T and vibrational-electronic modes at T_v), $\boldsymbol{e}^* = (e_v)$, and $\boldsymbol{T}^* = (T_v)$. Finally, three-temperature models have $T \neq T_r \neq T_v$, $\boldsymbol{e}^* = (e_r, e_v)$, and $\boldsymbol{T}^* = (T_r, T_v)$.

To generalize our results over the number of modeled energy modes, it will be convenient to use the matrix $\mathrm{E}^{*,\mathsf{T}} \in \mathbb{R}^{(n_t-1)\times n_c}$ defined as

$$\mathrm{E}^{*,\mathsf{T}} = \begin{bmatrix} e_{r,1} & e_{r,2} & \cdots & e_{r,n_c} \\ e_{v,1} & e_{v,2} & \cdots & e_{v,n_c} \\ \vdots & \vdots & \ddots & \vdots \end{bmatrix}, \tag{32}$$

where a row is included only when the energy mode is modeled with its own temperature. For example, in a two temperature model, $\mathrm{E}^{*,\mathsf{T}}$ is effectively a row vector containing only the species vibrational energies. $\mathrm{E}^{*,\mathsf{T}}$ for a three temperature model with a single rotational mode and single vibrational mode would be the first two rows of the generic form above. For a system with n_{vib} vibration and n_{rot} rotation modes, this matrix could take the form

$$\mathrm{E}^{*,\mathsf{T}} = \begin{bmatrix} e_{r,1,1} & e_{r,1,2} & \cdots & e_{r,1,n_c} \\ e_{r,2,1} & e_{r,2,2} & \cdots & e_{r,2,n_c} \\ \vdots & \vdots & \ddots & \vdots \\ e_{r,n_{\text{rot}},1} & e_{r,n_{\text{rot}},2} & \cdots & e_{r,n_{\text{rot}},n_c} \\ e_{v,1,1} & e_{v,1,2} & \cdots & e_{v,1,n_c} \\ e_{v,2,1} & e_{v,2,2} & \cdots & e_{v,2,n_c} \\ \vdots & \vdots & \ddots & \vdots \\ e_{v,n_{\text{vib}},1} & e_{v,n_{\text{vib}},2} & \cdots & e_{v,n_{\text{vib}},n_c} \end{bmatrix}, \tag{33}$$

where $e_{x,y,z}$ is the energy of species z in mode number y of type x (rotational or vibrational).

3.3.3. Calorically vs Thermally Perfect Gases

A common assumption in aerodynamics is that air behaves as a *calorically perfect* gas with no excitation of vibrational molecular energy, which is valid under temperatures of around 600 K [1]. Both (26) and (31) represent a *thermally perfect* species whose heat capacity varies with temperature. The modally decomposed energy, (31), may be simplified to a calorically perfect form by simply removing the vibrational energy contribution and writing $T_r = T$ as a multitemperature calorically perfect model does not make sense.

3.4. Source Terms

The source terms in (1) for hypersonic flight consist of mass exchanges between components via chemical reactions and energy exchanges via excitation/relaxation of internal energy modes,

$$\boldsymbol{r}^{\mathsf{T}} = \left(\boldsymbol{r}_c^{\mathsf{T}}, \boldsymbol{0}, 0, \left(\boldsymbol{Q}^* + \mathrm{E}^{*,\mathsf{T}}\boldsymbol{r}_c\right)^{\mathsf{T}}\right), \tag{34}$$

where $\boldsymbol{r}_c \in \mathbb{R}^{n_c}$ is the vector of specific, net component production rates and $\boldsymbol{Q}^* \in \mathbb{R}^{n_t-1}$ is the vector of net excitation rates of the internal energy modes. Chemical reaction rates are typically modeled with Arrhenius-form rate constants and the law of mass action [1], while the energy relaxation rates are often written [1, 25] in terms of a relaxation time and the difference between the equilibrium energy value (*e.g.*, e_v evaluated at T) and instantaneous value (*e.g.*, e_v evaluated at $T_v \neq T$).

3.5. Flux Vectors

The inviscid and viscous fluxes in direction x_k are given below. In direction x_k, $\boldsymbol{j}^{x_k} \in \mathbb{R}^{n_c}$ is the vector of component mass diffusive fluxes relative to the mass-averaged velocity, $\mathfrak{q}^{x_k}_{\text{total}} \in \mathbb{R}$ is the total conductive heat flux, $\boldsymbol{\mathsf{q}}^{*,x_k} \in \mathbb{R}^{n_t-1}$ is the vector of internal mode conductive heat fluxes, $\boldsymbol{h} \in \mathbb{R}^{n_c}$ is the vector of specific, component internal enthalpies, υ^{x_k} is the velocity projected in x_k, $\boldsymbol{n}_k$ is a unit vector in the x_k direction, and $\tau \in \mathbb{R}^{n_d \times n_d}$ is the matrix of viscous stresses.

$$\boldsymbol{f}^{x_k} = \begin{pmatrix} \upsilon^{x_k}\boldsymbol{\rho} \\ \upsilon^{x_k}\rho\boldsymbol{\upsilon} + p\boldsymbol{n}_k \\ \upsilon^{x_k}(\rho E + p) \\ \upsilon^{x_k}\rho\boldsymbol{e}^* \end{pmatrix}, \qquad \boldsymbol{f}^{v,x_k} = \underbrace{\begin{pmatrix} \boldsymbol{0} \\ \tau\boldsymbol{n}_k \\ \boldsymbol{\upsilon}^{\mathsf{T}}\tau\boldsymbol{n}_k \\ \boldsymbol{0} \end{pmatrix}}_{\text{momentum}} - \underbrace{\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \boldsymbol{0} \\ \mathsf{q}^{x_k}_{\text{total}} + \boldsymbol{h}^{\mathsf{T}}\boldsymbol{j}^{x_k} \\ \boldsymbol{\mathsf{q}}^{*,x_k} + \mathrm{E}^{*,\mathsf{T}}\boldsymbol{j}^{x_k} \end{pmatrix}}_{\text{mass, energy}}. \tag{35}$$

The symmetric viscous stress matrix for a Newtonian fluid with viscosity μ_{visc} and dilational viscosity λ_{visc} is

$$\tau_{i,j} = \delta_{i,j}\lambda_{\text{visc}} \sum_{i=1}^{n_d} \upsilon^{x_i}_{x_i} + \mu_{\text{visc}} \left(\upsilon^{x_i}_{x_j} + \upsilon^{x_j}_{x_i} \right), \tag{36}$$

and the total conductive heat flux is

$$\mathsf{q}^{x_k}_{\text{total}} = \mathsf{q}^{x_k}_t + \boldsymbol{1}^{\mathsf{T}}\boldsymbol{\mathsf{q}}^{*,x_k}, \tag{37}$$

in which $\mathsf{q}^{x_k}_t$ is the translational mode conductive heat flux.

We identify the $\mathrm{C}_{i,j}$ matrices in Definition 2.1 for the viscous fluxes by splitting into momentum ($\boldsymbol{f}^{v,x_k}_{\text{mom}}$) and mass/energy fluxes ($\boldsymbol{f}^{v,x_k}_{\text{me}}$). The $\mathrm{C}_{i,j}$ matrices for momentum are all nonzero, while those of the mass and energy fluxes are nonzero only on the diagonal, as shown below for a three-dimensional case.

$$\begin{aligned} \begin{pmatrix} \boldsymbol{f}^{v,x_1} \\ \boldsymbol{f}^{v,x_2} \\ \boldsymbol{f}^{v,x_3} \end{pmatrix} &= \boldsymbol{f}^{v,x_k}_{\text{mom}} - \boldsymbol{f}^{v,x_k}_{\text{me}}, \\ &= \left(\begin{bmatrix} \hat{\mathrm{C}}_{\text{mom},1,1} & \hat{\mathrm{C}}_{\text{mom},1,2} & \hat{\mathrm{C}}_{\text{mom},1,3} \\ \hat{\mathrm{C}}_{\text{mom},2,1} & \hat{\mathrm{C}}_{\text{mom},2,2} & \hat{\mathrm{C}}_{\text{mom},2,3} \\ \hat{\mathrm{C}}_{\text{mom},3,1} & \hat{\mathrm{C}}_{\text{mom},3,2} & \hat{\mathrm{C}}_{\text{mom},3,3} \end{bmatrix} - \begin{bmatrix} \hat{\mathrm{C}}_{\text{me},1,1} & & \\ & \hat{\mathrm{C}}_{\text{me},2,2} & \\ & & \hat{\mathrm{C}}_{\text{me},3,3} \end{bmatrix} \right) \begin{pmatrix} \boldsymbol{w}_{x_1} \\ \boldsymbol{w}_{x_2} \\ \boldsymbol{w}_{x_3} \end{pmatrix}. \end{aligned} \tag{38}$$

The general case is

$$\boldsymbol{f}^{v,x_k} = \boldsymbol{f}^{v,x_k}_{\text{mom}} - \boldsymbol{f}^{v,x_k}_{\text{me}} = \sum_{j=1}^{n_d} \hat{\mathrm{C}}_{\text{mom},k,j}\boldsymbol{w}_{x_j} - \hat{\mathrm{C}}_{\text{me},\alpha,\alpha}\boldsymbol{w}_{x_\alpha}. \tag{39}$$

where $\hat{\mathrm{C}}_{\text{me},\alpha,\alpha}$ is the (α, α) diagonal entry of the block diagonal mass/energy matrix (note that Greek subscripts are used to indicate that indices are *not* summed over as in Einstein notation). The viscous momentum fluxes are given above in the standard form for Newtonian fluids, and the requirements on the momentum fluxes for entropy stability are not affected by thermochemical nonequilibrium. Stability requires $\mu_{\text{visc}} \geq 0$ and $\lambda_{\text{visc}} + \frac{2}{3}\mu_{\text{visc}} \geq 0$ as shown by Hauke et al. [14] for a single-component, single-temperature ideal gas and Chalot et al. [5] for multicomponent mixtures with two temperatures. We refer the reader to these articles [5, 14] for details regarding stability of the viscous momentum fluxes.

In contrast to the momentum fluxes, the mass and energy fluxes have been calculated in many ways (see, for instance, Coffee and Heimerl [7], Bird, Stewart, and Lightfoot [2], or Taylor and Krishna [23]). These include complicated models grounded in irreversible thermodynamics and simpler models such as Fick's law with unity Lewis numbers or mixture-averaged diffusion coefficients. Computing and enforcing conditions on the $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ matrix is quite complicated and is an important aspect of extending entropy stability proofs to multicomponent flows. We next write a general formulation to assist in verifying the provable stability of various diffusion models and also identify an alternative method of *constructing* entropy-stable fluxes.

3.6. Entropy Stable Diffusion Models

We first write the contribution of mass and energy fluxes to the total viscous flux vector in terms of $\boldsymbol{j}^{x_k}$, $\mathfrak{q}_t^{x_k}$, $\boldsymbol{\mathfrak{q}}^{*,x_k}$, and the N matrix defined below.

$$\boldsymbol{f}_{\mathrm{me}}^{v,x_k} = \begin{pmatrix} \boldsymbol{j}^{x_k} \\ \mathbf{0} \\ \mathfrak{q}_{\mathrm{total}}^{x_k} + \boldsymbol{h}^{\mathsf{T}}\boldsymbol{j}^{x_k} \\ \boldsymbol{\mathfrak{q}}^{*,x_k} + \mathrm{E}^{*,\mathsf{T}}\boldsymbol{j}^{x_k} \end{pmatrix} = \mathrm{N}\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \mathbf{0} \\ \mathfrak{q}_t^{x_k} \\ \boldsymbol{\mathfrak{q}}^{*,x_k} \end{pmatrix}, \quad \mathrm{N} = \begin{bmatrix} \mathrm{I} & 0 & 0 & 0 \\ 0 & \mathrm{I} & 0 & 0 \\ \boldsymbol{h}^{\mathsf{T}} & 0 & 1 & \mathbf{1}^{\mathsf{T}} \\ \mathrm{E}^{*,\mathsf{T}} & 0 & 0 & \mathrm{I} \end{bmatrix}. \tag{40}$$

Next, the fluxes are written in terms of a general A matrix, consisting of diffusion coefficients, thermal conductivities, and state transformations, and the primitive variable gradients, which we then transform to entropy variable gradients as in Definition 2.1,

$$\boldsymbol{f}_{\mathrm{me}}^{v,x_k} = \mathrm{N}\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \mathbf{0} \\ \mathfrak{q}_t^{x_k} \\ \boldsymbol{\mathfrak{q}}^{*,x_k} \end{pmatrix} = -\mathrm{N}\mathrm{A}\boldsymbol{v}_{x_k} = -\mathrm{N}\mathrm{A}\boldsymbol{v}_{\boldsymbol{w}}\boldsymbol{w}_{x_k}, \tag{41}$$

which yields

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \mathrm{N}\mathrm{A}\boldsymbol{v}_{\boldsymbol{w}}. \tag{42}$$

The fact that $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ must be symmetric and positive-semidefinite (SPSD) leads to conditions on the A matrix that converts gradients of primitive variables into the fluxes $\boldsymbol{j}^{x_k}$, $\mathfrak{q}_t^{x_k}$, $\boldsymbol{\mathfrak{q}}^{*,x_k}$. Furthermore, we might additionally consider designing the entropy function to alter the $\boldsymbol{v}_{\boldsymbol{w}}$ matrix to aid in satisfying conditions on $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$. However this appears impractical and unlikely to succeed, so we translate conditions on $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ to the A matrix alone.

Given a diffusion model, we can identify its A matrix by rewriting it in terms of gradients of the primitive variables. Then checking its $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ matrix as above would inform one whether or not it is provably entropy stable. Chalot et al. [5] perform this for a rigorous diffusion model grounded in irreversible thermodynamics and demonstrates that the $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ is SPSD given that the diffusion model satisfies the second law of thermodynamics.

3.6.1. Entropy Stable Fluxes by Construction

An interesting alternative to checking the provable entropy stability of a given diffusion model is to *construct* an entropy stable A matrix, A^S, as follows, with any SPSD matrix G,

$$\mathrm{A}^S = \mathrm{G}\mathrm{N}^\mathsf{T}\boldsymbol{w}_{\boldsymbol{v}}, \tag{43}$$

as this produces an SPSD $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ matrix because G is SPSD and N has full rank,

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \mathrm{N}\mathrm{G}\mathrm{N}^\mathsf{T}\boldsymbol{w}_{\boldsymbol{v}}\boldsymbol{v}_{\boldsymbol{w}} = \mathrm{N}\mathrm{G}\mathrm{N}^\mathsf{T}. \tag{44}$$

3.6.2. Simple Diffusion Model

A simple formulation of the diffusion fluxes involving Fick's Law and Fourier's Law is given below, wherein $\boldsymbol{Y} = \boldsymbol{\rho}/\rho$ is the vector of component mass fractions constrained to the simplex in $(0,1)^{n_c}$ on which $\mathbf{1}^\mathsf{T}\boldsymbol{Y} = 1$, $\boldsymbol{D} \in (\mathbb{R}^+)^{n_c}$ is the vector of component diffusion coefficients, $\kappa \in \mathbb{R}^+$ is the thermal conductivity of the translational and equilibrated modes, and $\boldsymbol{\kappa}^* \in (\mathbb{R}^+)^{n_t-1}$ is the vector of internal mode thermal conductivities.

$$\begin{aligned} \boldsymbol{j}^{x_k} &= -\rho\,\mathrm{diag}(\boldsymbol{D})\boldsymbol{Y}_{x_k}, \\ \mathfrak{q}_t^{x_k} &= -\kappa T_{x_k}, \\ \boldsymbol{\mathfrak{q}}^{*,x_k} &= -\mathrm{diag}(\boldsymbol{\kappa}^*)\boldsymbol{T}^*_{x_k}, \end{aligned} \tag{45}$$

The diffusion coefficients can be computed by assuming that each species has a particular Lewis number or with a mixture-averaged diffusion approach. This formulation is simple and incorporates no coupling between components and temperatures (*e.g.*, the Soret and Dufour effects).

3.6.3. Rigorous Diffusion Model

In contrast to the simple diffusion model, we now present a more complex framework grounded in irreversible thermodynamics. This model involves the diffusional driving force vector $\boldsymbol{d}^{x_k} \in \mathbb{R}^{n_c}$ which includes the mole fractions $\boldsymbol{X}_k \in (0,1)^{n_c} : \mathbf{1}^\mathsf{T}\boldsymbol{X} = 1$. We derived this form by following Bird et al. [2] and incorporating entropy generation due to thermal excitation [25], which yields the $T\mathrm{diag}(\boldsymbol{T}^*)^{-1}$ term (*e.g.*, T/T_v) in the internal mode driving force.

$$\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \mathfrak{q}_t^{x_k} \\ \boldsymbol{\mathfrak{q}}^{*,x_k} \end{pmatrix} = -\mathcal{L}\begin{pmatrix} R_{\mathrm{mix}}T\mathrm{diag}(\boldsymbol{Y})^{-1}\boldsymbol{d}^k \\ (\ln T)_{x_k} \\ T\mathrm{diag}(\boldsymbol{T}^*)^{-1}(\ln \boldsymbol{T}^*)_{x_k} \end{pmatrix}, \tag{46}$$

$$\boldsymbol{d}^{x_k} = \boldsymbol{X}_{x_k} + (\boldsymbol{X} - \boldsymbol{Y})(\ln p)_{x_k}. \tag{47}$$

The model above includes gradient-driven diffusion, barometric (pressure) diffusion, multicomponent coupling between components, and Soret/Dufour coupling between components and heat. We partition the phenomenological coefficient matrix into $\mathcal{L}^{\mathrm{c,c}}$, a symmetric component-component coupling block,

$\mathcal{L}_{t,t}$, the translational mode diagonal coefficient, $\mathcal{L}^{*,*}$, the diagonal matrix of internal mode coefficients, and the Soret flux coefficients (with Dufour terms on the transpose) $\boldsymbol{\mathcal{L}}^{c,t}$ as shown below.

$$\mathcal{L} = \begin{bmatrix} \mathcal{L}^{\mathrm{c,c}} & \boldsymbol{\mathcal{L}}^{c,t} & 0 \\ & \mathcal{L}_{t,t} & 0 \\ \text{sym.} & & \mathcal{L}^{*,*} \end{bmatrix}. \tag{48}$$

Dependence of the species fluxes gives the following conditions on the phenomenological coefficients:

$$\begin{aligned} \mathcal{L}^{\mathrm{c,c}}\mathbf{1} &= \mathbf{0}, \\ \mathbf{1}^{\mathsf{T}}\boldsymbol{\mathcal{L}}^{c,t} &= 0. \end{aligned} \tag{49}$$

The Onsager Reciprocal Relations further require that the $\mathcal{L}$ matrix is symmetric, and the second law of thermodynamics requires that $\mathcal{L}$ is positive semi-definite.

We note that because we restrict $\mathcal{L}^{*,*}$ to be diagonal each of the internal mode heat fluxes (for example, the vibrational mode) in (46) take the form

$$\boldsymbol{q}_{v,x_k} = -\mathcal{L}^{v,v}\frac{T}{T_v}(\ln T_v)_{x_k} = -\mathcal{L}^{v,v}\frac{T}{T_v^2}T_{v,x_k}. \tag{50}$$

Comparison to a form with thermal conductivities in (45) shows that the conductivities relate to the phenomenological coefficients as

$$\kappa_v = \mathcal{L}^{v,v}T. \tag{51}$$

4. ENTROPY FUNCTIONS AND STABILITY FOR THERMOCHEMICAL NONEQUILIBRIUM SYSTEMS

In this section we derive entropy functions for ideal gases in thermochemical nonequilibrium and resultant requirements on diffusion models and source terms. This section establishes continuous entropy stability and §5 extends this to the semi-discrete case. Section 4.1 derives thermodynamic entropy functions for several types of mixtures as the basis for stability proofs in §4.2 and §4.3.

4.1. Thermodynamic Entropy Functions

4.1.1. One-Temperature Mixtures

We begin with a single-temperature mixture of ideal gases. The entropy of a closed subsystem in thermal equilibrium and consisting only of component j satisfies the differential relation

$$\mathrm{d}s_j = -\frac{R_j}{\rho_j}\mathrm{d}\rho_j + \frac{c_{v,j}}{T}\mathrm{d}T, \tag{52}$$

which we can integrate from the reference state with entropies s_j° and densities ρ_j°

$$s_j = s_j^\circ + R_j \ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + \int_{T^\circ}^{T} \frac{c_{v,j}}{T} \mathrm{d}T. \tag{53}$$

The mixture entropy is then simply the mass-weighted average of the species entropies,

$$\rho s = \sum_{i=1}^{n_c} \rho_j s_j^\circ + \sum_{i=1}^{n_c} \rho_j R_j \ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + \sum_{i=1}^{n_c} \rho_j \int_{T^\circ}^{T} \frac{c_{v,j}}{T} \mathrm{d}T. \tag{54}$$

At this point we specify the heat capacity with either the polynomial approach (§3.3.1) or the modal energy decomposition (§3.3.2). The isochoric heat capacity from NASA polynomials is given in (25) and its integral yields

$$s_j = s_j^\circ + R_j \left[\ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + (a_{j,1} - 1)\ln T + a_{j,2} T + \frac{a_{j,3}}{2} T^2 + \frac{a_{j,4}}{3} T^3 + \frac{a_{j,5}}{4} T^4\right]. \tag{55}$$

From the modal energy decomposition we have

$$c_{v,j} = c_{v,t,j} + c_{v,r,j} + c_{v,v,j} = \frac{3 + 2\nu_i}{2} R_i + \nu_i e_{v,i}^2 \frac{\exp(\Theta_i / T_v)}{R_i T_v^2}. \tag{56}$$

In the approximation of calorically perfect gases, valid at low temperatures only, the vibrational term is dropped and the species entropy is

$$s_j = s_j^\circ + R_j \left[\ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + \frac{3 + 2\nu_i}{2} \ln\left(\frac{T}{T^\circ}\right)\right] \quad \text{(calorically perfect)}. \tag{57}$$

In the more general thermally perfect model we include the vibrational energy and obtain

$$\begin{aligned} s_j =& s_j^\circ + R_j \left[\ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + \frac{3 + 2\nu_i}{2} \ln\left(\frac{T}{T^\circ}\right)\right] + \\ \nu_j & \left(\frac{e^{\Theta_j/T}}{T} e_{v,j}(T) - \frac{e^{\Theta_j/T^\circ}}{T^\circ} e_{v,j}(T^\circ) - R_j \ln\left[\frac{e^{\Theta_j/T} - 1}{e^{\Theta_j/T^\circ} - 1}\right]\right). \end{aligned} \tag{58}$$

4.1.2. Multitemperature Mixtures

When thermal nonequilibrium exists we expand our thermodynamic system to incorporate co-extensive subsystems [25] for the internal energy modes not in equilibrium with the translational mode. Entropy is generated by the heat fluxes between these modes. We follow classical approaches [25] and restrict internal heat fluxes to those between internal mode and the translational mode, and furthermore allow external heat fluxes only with the translational subsystem. The application of differential energy and entropy balances to each energy mode then yields the following differential expression of the energy of species j.

$$\mathrm{d}s_j = \frac{R_j}{\rho_j} \mathrm{d}\rho_j + \frac{c_{v,t,j}}{T} \mathrm{d}T + \sum_{e \in \mathcal{E}} \frac{c_{v,e,j}}{T_e} \mathrm{d}T_e, \tag{59}$$

where $\mathcal{E}$ is the set of internal modes modeled with their own temperature. Following the prior section and maintaining separate temperatures for the translational, rotational, and vibrational-electronic modes yields

$$\begin{aligned} s_j =& s_j^\circ + R_j \left[\ln\left(\frac{\rho_j^\circ}{\rho_j}\right) + \frac{3}{2}\ln\left(\frac{T}{T^\circ}\right) + \nu_j \ln\left(\frac{T_r}{T^\circ}\right)\right] + \\ & \nu_j \left(\frac{e^{\Theta_j/T_v}}{T_v} e_{v,j}(T_v) - \frac{e^{\Theta_j/T^\circ}}{T^\circ} e_{v,j}(T^\circ) - R_j \ln\left[\frac{e^{\Theta_j/T_v}-1}{e^{\Theta_j/T^\circ}-1}\right]\right). \end{aligned} \tag{60}$$

The above result is appropriate for a three-temperature model and may be directly simplified to two- and one-temperature models by setting the appropriate temperature(s) equal to T, ultimately reducing (60) to (58).

4.2. Entropy Stability for One-Temperature Mixtures

Equipped with the thermodynamic entropy functions of §4.1 we are now capable of proving entropy stability for the continuous problem, (1), for mixtures in thermochemical nonequilibrium. We begin in this section with one-temperature models. Theorem 1 first establishes conditions for entropy stability. These are shown in Theorem 2 to require that the mass diffusion model in a provably entropy stable system is strictly conservative of the total mass.

Theorem 1. The negative of the volumetric thermodynamic entropy of the mixture, $\mathcal{S} = -\boldsymbol{\rho}^\mathsf{T}\boldsymbol{s}$, is an entropy function of (1) for one-temperature, multicomponent flows as defined in Definition 2.1 under the following conditions.

1. The temperature is strictly positive, $T > 0$.
2. The isochoric heat capacity of the mixture is strictly positive, $c_v > 0$.
3. Component densities are strictly positive, $\rho_i > 0 \, \forall i$.
4. The viscosity is nonnegative, $\mu_\text{visc} \geq 0$ and satisfies $\lambda_\text{visc} + \frac{2}{3}\mu_\text{visc} \geq 0$, where λ_visc is the dilatational viscosity.
5. The chemical reaction mechanism is consistent with the second law of thermodynamics.
6. The mass and energy diffusive fluxes, when written as

$$\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \mathbf{0} \\ \mathfrak{q}^{x_k} \end{pmatrix} = - \begin{bmatrix} \mathrm{A}_1 & 0 & \boldsymbol{a}_2 \\ 0 & 0 & 0 \\ \boldsymbol{a}_3^\mathsf{T} & 0 & a_4 \end{bmatrix} \begin{pmatrix} \boldsymbol{\rho}_{x_k} \\ \boldsymbol{v}_{x_k} \\ T_{x_k} \end{pmatrix} = -\mathrm{A}\boldsymbol{v}_{x_k}, \tag{61}$$

   for submatrices A_1, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$, and a_4 are determined by the diffusion model satisfies the symmetry conditions, wherein $\zeta_i = \rho_i/R_i$,

   a) $\mathrm{A}_1 \mathrm{diag}(\boldsymbol{\zeta})$ is symmetric
   b) $\mathrm{A}_1\boldsymbol{\zeta} = 0$
   c) $\boldsymbol{a}_3^\mathsf{T}\boldsymbol{\zeta} = 0$

d) $\mathrm{A}_1\boldsymbol{\rho}T + \mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{a}_3 = \boldsymbol{a}_2T^2$

and produces a symmetric, positive semidefinite $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \mathrm{NA}\boldsymbol{v}_{\boldsymbol{w}}$ matrix.

Proof. The entropy variables corresponding to the function $\mathcal{S} = -\boldsymbol{\rho}^\mathsf{T}\boldsymbol{s}$ are

$$\boldsymbol{w} = \left(\frac{\partial \mathcal{S}}{\partial \boldsymbol{q}}\right)^\mathsf{T} = \frac{1}{T}\begin{pmatrix} \boldsymbol{\mu} - \frac{1}{2}\boldsymbol{v}^\mathsf{T}\boldsymbol{v} \\ \boldsymbol{v} \\ -1 \end{pmatrix}, \tag{62}$$

where the species specific chemical potentials are $\boldsymbol{\mu} = \boldsymbol{e}_{\mathrm{total}} + (\boldsymbol{R} - \boldsymbol{s})T$. Following Definition 2.1, we first verify the compatibility relation, $\mathcal{S}_{\boldsymbol{q}}\boldsymbol{f}^{x_i}_{x_i} = \mathcal{F}^{x_i}_{x_i}$. With the entropy flux, $\mathcal{F}^{x_i} = v^{x_i}\mathcal{S}$, we derive the entropy potential flux, $\psi^{x_i} = v^{x_i}\boldsymbol{\rho}^\mathsf{T}\boldsymbol{R}$, and find that the compatibility relation holds.

Next we show that the Hessian matrix $\mathcal{S}_{\boldsymbol{qq}}$ is symmetric positive definite. The inverse of the Hessian matrix, identified to be symmetric, is

$$\mathcal{S}_{\boldsymbol{qq}}^{-1} = \boldsymbol{q}_{\boldsymbol{w}} = \begin{bmatrix} \mathrm{diag}(\boldsymbol{\zeta}) & \boldsymbol{\zeta}\boldsymbol{v}^\mathsf{T} & \mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{E} \\ & \boldsymbol{1}^\mathsf{T}\boldsymbol{\zeta}\boldsymbol{v}\boldsymbol{v}^\mathsf{T} + \rho T\mathrm{I} & \boldsymbol{v}\boldsymbol{1}^\mathsf{T}\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{E} + \rho T\boldsymbol{v} \\ \text{sym.} & & (\boldsymbol{q}_{\boldsymbol{w}})_{3,3} \end{bmatrix}, \tag{63}$$

where $\zeta_i = \rho_i/R_i$ and the unspecified element is:

$$(\boldsymbol{q}_{\boldsymbol{w}})_{3,3} = \boldsymbol{E}^\mathsf{T}\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{E} + \rho T\boldsymbol{v}^\mathsf{T}\boldsymbol{v} + \rho c_v T^2, \tag{64}$$

The Hessian matrix is diagonalized by

$$\mathcal{S}_{\boldsymbol{qq}} = \boldsymbol{q}_{\boldsymbol{v}} \begin{bmatrix} \mathrm{diag}(\boldsymbol{\zeta}) & & \\ & \frac{T}{\rho}\mathrm{I} & \\ & & \frac{T^2}{\rho c_v} \end{bmatrix} \boldsymbol{q}_{\boldsymbol{v}}^\mathsf{T}, \tag{65}$$

demonstrating the it is both symmetric and positive definite given the positivity of temperature, the heat capacity, and component densities ($\zeta_i = \rho_i/R_i > 0 \rightarrow \rho_i > 0$). Thus, the Hessian is symmetric positive definite.

Conditions on the diffusion model arise out of the required symmetry and positive semi-definiteness of the viscous flux Jacobian matrices in terms of the entropy variables,

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \mathrm{NA}\boldsymbol{v}_{\boldsymbol{w}}. \tag{66}$$

Direct computation of this matrix for the given entropy variables (62) yields

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \begin{bmatrix} \mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta}) & \mathrm{A}_1\boldsymbol{\zeta}\boldsymbol{v}^\mathsf{T} & \mathrm{A}_1\boldsymbol{\zeta}\frac{\boldsymbol{v}^\mathsf{T}\boldsymbol{v}}{2} + \mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{e} + T^2\boldsymbol{a}_2 \\ 0 & 0 & 0 \\ \left(\boldsymbol{h}^\mathsf{T}\mathrm{A}_1 + \boldsymbol{a}_3^\mathsf{T}\right)\mathrm{diag}(\boldsymbol{\zeta}) & \left(\boldsymbol{h}^\mathsf{T}\mathrm{A}_1 + \boldsymbol{a}_3^\mathsf{T}\right)\boldsymbol{\zeta}\boldsymbol{v}^\mathsf{T} & \left(\boldsymbol{h}^\mathsf{T}\mathrm{A}_1 + \boldsymbol{a}_3^\mathsf{T}\right)(\zeta\frac{\boldsymbol{v}^\mathsf{T}\boldsymbol{v}}{2} + \mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{e}) + \\ & & (\boldsymbol{h}^\mathsf{T}\boldsymbol{a}_2 + a_4)T^2 \end{bmatrix}. \tag{67}$$

The given constraints (6a)-(6d) arise directly out of the requirements of symmetry and positive semi-definiteness. With the symmetry conditions on (61) satisfied, the matrix simplifies to

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \begin{bmatrix} \mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta}) & 0 & \mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{h} + \mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{a}_3 \\ 0 & 0 & 0 \\ (\mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{h} + \mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{a}_3)^\mathsf{T} & 0 & \boldsymbol{h}^\mathsf{T}\mathrm{A}_1\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{h} + a_4T^2 + (2\boldsymbol{h} - \boldsymbol{R}T)^\mathsf{T}\mathrm{diag}(\boldsymbol{\zeta})\boldsymbol{a}_3 \end{bmatrix}, \tag{68}$$

which may be evaluated for positive semi-definiteness for a given diffusion model.

Finally we assess the entropy source term, $\mathcal{R} = \boldsymbol{w}^\mathsf{T}\boldsymbol{r}$, which must be negative semi-definite for entropy stability. For $\boldsymbol{r}$ defined in (34), we have

$$\mathcal{R} = \frac{1}{T}\boldsymbol{\mu}^\mathsf{T}\boldsymbol{r}_c = \frac{1}{T}\sum_{j=1}^{n_r}\Delta\mu_j\xi_j, \tag{69}$$

where $\Delta\mu_j$ is the change in Gibbs free energy due to reaction j, ξ_j is the rate of progress of reaction j, and n_r is the number of chemical reactions, is the vector of specific component Gibbs free energies. At chemical equilibrium $\mathcal{R} = 0$ as $\xi_j = 0,\ \forall j$. Away from equilibrium $\mathcal{R}$ is negative semi-definite provided the reaction mechanism is consistent with the second law of thermodynamics. □

Theorem 2. The conditions given in Theorem 1 require that the mass diffusion model strictly conserve mass.

Proof. Conservation of mass requires that the diffusive fluxes satisfy $\mathbf{1}^\mathsf{T}\boldsymbol{j}_{x_k} = 0$ for all directions. The form of the mass diffusive fluxes in Theorem 1 yields

$$\mathbf{1}^\mathsf{T}\boldsymbol{j}_{x_k} = -\mathbf{1}^\mathsf{T}\mathrm{A}_1\boldsymbol{\rho}_{x_k} - \mathbf{1}^\mathsf{T}\boldsymbol{a}_2T_{x_k}. \tag{70}$$

Condition (6a) and (6b) yield $\mathbf{1}^\mathsf{T}\mathrm{A}_1 = 0$ while (6c) and (6d) yield $\mathbf{1}^\mathsf{T}\boldsymbol{a}_2 = 0$. Thus the sum of the diffusive fluxes is identically zero and mass is conserved for a model that satisfies Theorem 1. □

Theorem 3. The diffusion model consistent with irreversible thermodynamics presented in §3.6.3 satisfies the conditions for entropy stability given in Theorem 1.

Proof. The diffusion model given by (46) and (47) with phenomenological coefficients satisfying (49) and the second law of thermodynamics ($\mathcal{L}$ is SPSD) can be written as in Theorem 1 with

$$\begin{aligned} \mathrm{A}_1 &= T\mathcal{L}^{\mathrm{c,c}}\mathrm{diag}(\boldsymbol{\zeta})^{-1}, \\ \boldsymbol{a}_2 &= \mathcal{L}^{\mathrm{c,c}}\boldsymbol{R} + T^{-1}\boldsymbol{\mathcal{L}}^{c,t}, \\ \boldsymbol{a}_3 &= T\mathrm{diag}(\boldsymbol{\zeta})^{-1}\boldsymbol{\mathcal{L}}^{c,t}, \\ a_4 &= \boldsymbol{R}^\mathsf{T}\boldsymbol{\mathcal{L}}^{c,t} + T^{-1}\mathcal{L}_{t,t}. \end{aligned} \tag{71}$$

Substitution verifies that the symmetry conditions are satisfied. Furthermore, with this model we find

$$\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha} = \mathrm{N}\mathcal{L}\mathrm{N}^\mathsf{T}, \tag{72}$$

which shows that $\hat{\mathrm{C}}_{\mathrm{me},\alpha,\alpha}$ is SPSD along with $\mathcal{L}$ due to the Onsager reciprocal relations and second law of thermodynamics. □

Theorem 4. The 'simple' diffusion model presented in §3.6.2 does not satisfy the conditions given in Theorem 1.

Proof. The diffusion model given by (45) can be written as in Theorem 1 with

$$\begin{aligned} \mathrm{A}_1 &= \mathrm{diag}(\boldsymbol{D})\mathrm{U}, \\ \boldsymbol{a}_2 &= 0, \\ \boldsymbol{a}_3 &= 0, \\ a_4 &= \kappa, \end{aligned} \tag{73}$$

where $\mathrm{U} = \mathrm{I} - \boldsymbol{Y}\mathbf{1}^{\mathsf{T}}$ is nonsymmetric, and singular because the mass fractions are dependent $(\mathbf{1}^{\mathsf{T}}\boldsymbol{Y} = 1)$. Substitution verifies that the symmetry conditions, (6a), (6b), and (6d), in Theorem 1 are not satisfied. □

Remark. The simple diffusion model, having been correctly identified as not conservative of mass when the diffusion coefficients vary ($\boldsymbol{D} \neq D\mathbf{1}$), has been used with the following correction [7, 20] to enforce mass conservation. After having computed the fluxes as in (45), they are corrected with

$$j_i^{x_k} = j_i^{x_k} - Y_i(\mathbf{1}^{\mathsf{T}}\boldsymbol{j}^{x_k}), \tag{74}$$

so that the sum after the correction is zero and mass is conserved. The matrix formulation of this correction approach is

$$\boldsymbol{j}^{x_k} = -\left(\mathrm{I} - \boldsymbol{Y}\mathbf{1}^{\mathsf{T}}\right)\rho\mathrm{diag}(\boldsymbol{D})\boldsymbol{Y}_{x_k} = -\mathrm{U}\mathrm{diag}(\boldsymbol{D})\mathrm{U}\boldsymbol{\rho}_{x_k}, \tag{75}$$

which does not satisfy the requirements given in Theorem 1. This shows that, while entropy stability leads to strict conservation of mass, conservation of mass does not lead to entropy stability.

Remark. Conservation of mass results from the symmetry and row sum property of the A_1 matrix that relates species density gradients to species diffusive fluxes in Theorem 1. Observe that if, as seen in the simple diffusion model (45), the off-diagonal vectors $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$ are zero, then condition (6d) of Theorem 1 requires $\mathrm{A}_1\boldsymbol{\rho} = 0$. Combined with the row sum property this implies that the rank of A_1 is at most $n_c - 2$, implying that there exists a second linear combination (in addition to total mass) of species gradients that yields zero diffusive flux of species, which is non-physical. Thus, a physically valid and entropy stable diffusion model will satisfy condition 6.4 without *both* of $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$ being zero, implying the requirement of barometric diffusion and/or coupled fluxes (the Soret/Dufour effects).

Remark. The following formulation of the species diffusive fluxes,

$$\begin{aligned} j_1^{x_k} &= -\rho\mathfrak{D}_1(d_1^{x_k} - Y_1/Y_{n_c}d_{n_c}^{x_k}), \\ j_2^{x_k} &= -\rho\mathfrak{D}_2(d_2^{x_k} - Y_2/Y_{n_c}d_{n_c}^{x_k}), \\ &\vdots, \\ j_{n_c-1}^{x_k} &= -\rho\mathfrak{D}_{n_c-1}(d_{n_c-1}^{x_k} - Y_{n_c-1}/Y_{n_c}d_{n_c}^{x_k}), \\ j_{n_c}^{x_k} &= -\sum_{i=1}^{n_c-1} j_i^{x_k}, \end{aligned} \tag{76}$$

for diffusion coefficients $\mathfrak{D}_i$ with units of length-squared per time, and with the heat flux,

$$\mathfrak{q}^{x_k} = -\kappa T_{x_k}, \tag{77}$$

can be proven entropy stable if $\mathfrak{D}_i \geq 0\,\forall i$ and $\kappa \geq 0$. This model fits into the framework of the formulation from irreversible thermodynamics in §3.6.3 and so Theorem 3 applies directly.

4.3. Entropy Stability for Multitemperature Mixtures

In this section we extend the results of §4.2 to multitemperature mixtures. Theorem 5 establishes the conditions for entropy stability for three-temperature mixtures, adding conditions on the internal mode thermal conductivities, heat capacities, and energy relaxation models ($\boldsymbol{Q}^*$ in (34)). As these conditions apply directly to two-temperature flows as well.

Theorem 5. The negative of the volumetric thermodynamic entropy of the mixture, $\mathcal{S} = -\boldsymbol{\rho}^\mathsf{T}\boldsymbol{s}$, is an entropy function of (1) for three-temperature, multicomponent flows as defined in Definition 2.1 under following conditions.

1. All temperatures are strictly positive, $T, T_r, T_v > 0$.
2. The isochoric heat capacity of each mode is strictly positive, $c_{v,t}, c_{v,r}, c_{v,v} > 0$.
3. Component densities are strictly positive, $\rho_i > 0\,\forall i$.
4. The viscosity is nonnegative, $\mu_\text{visc} \geq 0$ and satisfies $\lambda_\text{visc} + \frac{2}{3}\mu_\text{visc} \geq 0$, where λ_visc is the dilatational viscosity.
5. The chemical reaction mechanism is consistent with the second law of thermodynamics.
6. The thermal excitation model satisfies $\operatorname{sign}(Q_i^*) = \operatorname{sign}(T - T_i)$, $\forall i$.
7. The mass and energy diffusive fluxes, when written as

$$\begin{pmatrix} \boldsymbol{j}^{x_k} \\ \boldsymbol{0} \\ \mathfrak{q}^{x_k} \\ \mathfrak{q}_r^{x_k} \\ \mathfrak{q}_v^{x_k} \end{pmatrix} = -\begin{bmatrix} \mathrm{A}_1 & 0 & \boldsymbol{a}_2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ \boldsymbol{a}_3^\mathsf{T} & 0 & a_4 & 0 & 0 \\ 0 & 0 & 0 & \kappa_r & 0 \\ 0 & 0 & 0 & 0 & \kappa_v \end{bmatrix} \begin{pmatrix} \boldsymbol{\rho}_{x_k} \\ \boldsymbol{v}_{x_k} \\ T_{x_k} \\ T_{r,x_k} \\ T_{v,x_k} \end{pmatrix}, \tag{78}$$

   has nonnegative internal mode thermal conductivities, $\kappa_r, \kappa_v \geq 0$, and the mass and total energy diffusion matrix A satisfies the conditions of Theorem 1.

Proof. The entropy variables corresponding to the function $\mathcal{S} = -\boldsymbol{\rho}^\mathsf{T}\boldsymbol{s}$ are

$$\boldsymbol{w} = \left(\frac{\partial \mathcal{S}}{\partial \boldsymbol{q}}\right)^\mathsf{T} = \frac{1}{T}\begin{pmatrix} \boldsymbol{\mu} - \frac{1}{2}\boldsymbol{v}^\mathsf{T}\boldsymbol{v} \\ \boldsymbol{v} \\ -1 \\ 1 - T/T_r \\ 1 - T/T_v \end{pmatrix}, \tag{79}$$

where the species specific chemical potentials in this system exhibiting thermal non-equilibrium are

$$\boldsymbol{\mu} = \boldsymbol{e}_{\text{total}} + (\boldsymbol{R} - \boldsymbol{s})T + \boldsymbol{e}_r\left(\frac{T}{T_r} - 1\right) + \boldsymbol{e}_v\left(\frac{T}{T_v} - 1\right). \tag{80}$$

As in Theorem 1 we find that given these entropy variables the compatibility relation on the fluxes holds. The Hessian matrix for the three-temperature mixture can be diagonalized by

$$\mathcal{S}_{\boldsymbol{qq}} = \boldsymbol{q_v}\begin{bmatrix} \operatorname{diag}(\boldsymbol{\zeta}) & & & & \\ & \frac{T}{\rho}\mathrm{I} & & & \\ & & \frac{T^2}{\rho c_{v,t}} & & \\ & & & \frac{T_r^2}{\rho c_{v,r}} & \\ & & & & \frac{T_v^2}{\rho c_{v,v}} \end{bmatrix}\boldsymbol{q_v}^{\mathsf{T}}, \tag{81}$$

demonstrating that it is both symmetric and positive definite given the conditions enumerated above. Conditions on the diffusion model are straightforward to extend from those of Theorem 1 as the internal modes are not coupled. The entropy source term with internal energy relaxation is

$$\mathcal{R} = \sum_{j=1}^{n_r}\Delta g_j\xi_j + Q_v\left(\frac{1}{T} - \frac{1}{T_v}\right) + Q_r\left(\frac{1}{T} - \frac{1}{T_r}\right), \tag{82}$$

where Δg_j and ξ_j are given in Theorem 1. Negative definiteness now requires not only that the reaction mechanism is consistent with the second law of thermodynamics but also that the energy flow via excitation/relaxation goes towards the lower temperature. Or, that $\operatorname{sign}(Q_i^*) = \operatorname{sign}(T - T_i),\ \forall i.$ $\square$

5. ENTROPY CONSERVATIVE FLUX FUNCTIONS IN CONSERVATION FORM

Having established entropy stability of the governing equations in continuous form we next consider their semi-discrete form described in §2.2. Provable semi-discrete stability requires that the mass matrix $\mathcal{P}$ is diagonal so that it commutes in the time derivative and source terms. Next, the proof requires that viscous fluxes are evaluated with gradients of the entropy variables $\boldsymbol{w}$ and the $\hat{\mathrm{C}}_{k,k}$ matrices given here for mass and energy fluxes and by others [5, 14] for the momentum diffusive fluxes. Finally, one must use a two-point entropy conservative flux function that satisfied the local condition,

$$(\boldsymbol{f}^{S,x_k})^{\mathsf{T}}\Delta\boldsymbol{w} = \Delta\psi^{x_k}. \tag{83}$$

Under these conditions the semi-discrete entropy equation (16) mimics the continuous form. The purpose of this section is to derive these fluxes for a variety of types of multicomponent, multitemperature mixtures.

5.1. An Automated Derivation Procedure

Following others [6, 16, 21, 26] we develop entropy conservative fluxes in terms of a parameter vector $\boldsymbol{\mathcal{Z}}$. Comparing the parameter vectors used in these papers demonstrates that (83) (a scalar equation on a vector of unknowns) admits multiple solutions based on the choice of $\boldsymbol{\mathcal{Z}}$. To optimize the derivation of fluxes that satisfy (83), which may require a guess-and-check procedure to find a valid parameter vector, for the varieties of reacting flows of interest, we've developed an automated procedure with the SageMath [24] code.

This procedure revolves around expanding $\Delta\boldsymbol{w}$ and $\Delta\psi^{x_k}$ in terms of $\Delta\boldsymbol{\mathcal{Z}}$. For example, consider the potential flux,

$$\Delta\psi^{x_k} = \Delta(v^{x_k}\boldsymbol{\rho}^\mathsf{T}\boldsymbol{R}) = \overline{v^{x_k}}(\Delta\boldsymbol{\rho})^\mathsf{T}\boldsymbol{R} + \overline{(\boldsymbol{\rho}^\mathsf{T}\boldsymbol{R})}\Delta v^{x_k}, \tag{84}$$

which can be decomposed as such due to the general identity $\Delta(ab) = \overline{a}\Delta b + \overline{b}\Delta a$ where $\overline{a} = (a_\ell + a_r)/2$ is the arithmetic average of the left and right values. This product rule identity and the linearity of the jump operator, $\Delta(a + b) = \Delta a + \Delta b$, allow considerable simplification of $\Delta\boldsymbol{w}$ and $\Delta\psi^{x_k}$ in terms of jumps of primitive variables. Further identities are necessary for complete expansion, such as the following for the jump of the inverse, $\Delta a^{-1} = -\Delta a/(2\overline{a}\breve{a})$, where $\breve{a} = a_r a_\ell/(a_r + a_\ell)$ is the harmonic average. Simplifying identities are not present for general nonlinear functions, however, motivating the 'logarithmic average' [16],

$$\Delta\ln(a) = \frac{\Delta a}{\widetilde{a}}, \quad \rightarrow \quad \widetilde{a} = \frac{\Delta a}{\Delta\ln(a)}. \tag{85}$$

The logarithmic average is only numerically stable [16] when $\widetilde{a}$ is evaluated directly for large $|\Delta a|$ and with an approximation (*e.g.*, Taylor series) for small $|\Delta a|$. Generally, we define the $\mathcal{H}$-average of a quantity ϕ with respect to a function $\mathcal{H}$, denoted $[\phi]_\mathcal{H}$, as

$$[\phi]_\mathcal{H} = \frac{\Delta\phi}{\Delta\mathcal{H}(\phi)}. \tag{86}$$

In the limit of $\Delta\phi \rightarrow 0$ the inverse $1/\phi_\mathcal{H}$ approaches the $\partial\mathcal{H}/\partial\phi$. Thus we can evaluate the $\mathcal{H}$-average as

$$\frac{1}{[\phi]_\mathcal{H}} = \begin{cases} \frac{\Delta\mathcal{H}(\phi)}{\Delta\phi}, & |\Delta\phi| \geq \delta, \\ \sum_{j=1}^{\theta} \frac{1}{j!}\frac{\partial^j\mathcal{H}}{\partial\phi^j}(\Delta\phi)^{j-1}, & |\Delta\phi| < \delta, \end{cases}, \tag{87}$$

where δ is large enough to avoid substantial roundoff errors and $\theta > 1$ is an integer describing how many terms to retain in the Taylor series. The optimal value of θ is the minimal one such that the approximation is valid to within roundoff error, which depends upon the function $\mathcal{H}$.

Given the availability of a specially-defined average such as $[\phi]_\mathcal{H}$, the interface jump of any nonlinear function in $\Delta\boldsymbol{w}$ and $\Delta\psi^{x_k}$ may be written in an expansion in terms of the parameter vector jumps, $\Delta\boldsymbol{\mathcal{Z}}$. This allows us to write the expansions in quasilinear form,

$$\begin{aligned} \Delta w_1 &= \mathrm{H}_{11}\Delta\mathcal{Z}_1 + \mathrm{H}_{12}\Delta\mathcal{Z}_2 + \cdots + \mathrm{H}_{1n}\Delta\mathcal{Z}_n, \\ \Delta w_2 &= \mathrm{H}_{21}\Delta\mathcal{Z}_1 + \mathrm{H}_{22}\Delta\mathcal{Z}_2 + \cdots + \mathrm{H}_{2n}\Delta\mathcal{Z}_n, \\ &\vdots \\ \Delta w_n &= \mathrm{H}_{n1}\Delta\mathcal{Z}_1 + \mathrm{H}_{n2}\Delta\mathcal{Z}_2 + \cdots + \mathrm{H}_{nn}\Delta\mathcal{Z}_n, \\ \Delta\psi^{x_k} &= g_1\Delta\mathcal{Z}_1 + g_2\Delta\mathcal{Z}_2 + \cdots + g_n\Delta\mathcal{Z}_n. \end{aligned} \tag{88}$$

Then substituting $\Delta \boldsymbol{w} = \mathrm{H}\Delta\boldsymbol{\mathcal{Z}}$ and $\Delta\psi^{x_k} = \boldsymbol{g}^\mathsf{T}\Delta\boldsymbol{\mathcal{Z}}$ into (83) and solving for the flux vector yields an entropy conservative flux

$$\boldsymbol{f}^{S,x_k} = (\mathrm{H}^\mathsf{T})^{-1}\boldsymbol{g}. \tag{89}$$

We assume that the H^T matrix is invertible, a condition met when there is a one-to-one relationship between $\boldsymbol{\mathcal{Z}}$ and the conserved or primitive variables (which have a one-to-one mapping to the entropy variables).

We note that in prior work [6, 16, 21, 26] this problem does not appear to be solved as a linear system. Instead, the algebraic system is solved manually for each choice of $\boldsymbol{\mathcal{Z}}$. Using SageMath [24] to automate jump decomposition, assembly, and solution of the linear system has enabled us to quickly test different choices of the parameter vector, deriving entropy conservative fluxes and verifying their consistency (13) with ease. Next we present a number of entropy conservative flux functions for a variety of multicomponent, multitemperature mixtures.

5.2. Flux Functions for One-Temperature Mixtures

5.2.1. Calorically Perfect Mixtures

First we consider the simplest case of a calorically perfect, one-temperature mixture. The thermodynamic entropy of each component is given in (57) and the internal energy is (31) *without* the vibrational energy. This model is of little practical interest because vibrational modes will be relevant above 600 K, below which chemical reactions are effectively frozen and there is little purpose of a multicomponent model. We present it here as a starting point for more complicated thermally perfect and multitemperature mixtures.

We identify that an appropriate parameter vector that yields the following entropy conservative and consistent flux function is

$$\boldsymbol{\mathcal{Z}} = \begin{pmatrix} \mathcal{Z}_{\boldsymbol{\rho}} \\ \mathcal{Z}_{\boldsymbol{v}} \\ \mathcal{Z}_T \end{pmatrix} = \begin{pmatrix} \boldsymbol{\rho} \\ \boldsymbol{v} \\ 1/T \end{pmatrix}. \tag{90}$$

The expansion matrix H^T and vector $\boldsymbol{g}$ are given below for direction $\boldsymbol{n} = (n_0, n_1, n_2)$ for a two-component, three-dimensional case. Extension to additional components follows the pattern seen here.

$$\mathrm{H}^\mathsf{T} = \begin{bmatrix} R_1/\widetilde{\rho}_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_2/\widetilde{\rho}_2 & 0 & 0 & 0 & 0 \\ -\overline{v}_0\overline{\mathcal{Z}}_T & -\overline{v}_0\overline{\mathcal{Z}}_T & \overline{\mathcal{Z}}_T & 0 & 0 & 0 \\ -\overline{v}_1\overline{\mathcal{Z}}_T & -\overline{v}_1\overline{\mathcal{Z}}_T & 0 & \overline{\mathcal{Z}}_T & 0 & 0 \\ -\overline{v}_2\overline{\mathcal{Z}}_T & -\overline{v}_2\overline{\mathcal{Z}}_T & 0 & 0 & \overline{\mathcal{Z}}_T & 0 \\ -\frac{\overline{\boldsymbol{v}^\mathsf{T}\boldsymbol{v}}}{2} + \omega_{\text{total},1} & -\frac{\overline{\boldsymbol{v}^\mathsf{T}\boldsymbol{v}}}{2} + \omega_{\text{total},2} & \overline{v}_0 & \overline{v}_1 & \overline{v}_2 & -1 \end{bmatrix}, \tag{91}$$

where

$$\omega_{\text{total},i} = e^\circ_{f,i} + \frac{3 + 2\nu_i}{2} R_i \left(\frac{1}{\widetilde{\mathcal{Z}}_T} - T^\circ \right), \tag{92}$$

$$\boldsymbol{g} = \begin{pmatrix} R_1 \overline{v}^n \\ R_2 \overline{v}^n \\ n_0 \overline{\rho R_{\text{mix}}} \\ n_1 \overline{\rho R_{\text{mix}}} \\ n_2 \overline{\rho R_{\text{mix}}} \\ 0 \end{pmatrix}. \tag{93}$$

The entropy conservative flux function is

$$\boldsymbol{f}^{S,n} = \begin{pmatrix} f_{m,i}^{S,n} \\ \overline{\boldsymbol{v}} f_{\text{mass}} + p^* \boldsymbol{n} \\ \sum_{i=1}^{n_c} f_{m,i}^{S,n} \omega_{\text{total},i} + p^* \overline{v}^n + \left(\overline{\boldsymbol{v}}^\mathsf{T} \overline{\boldsymbol{v}} - \frac{\overline{\boldsymbol{v}^\mathsf{T} \boldsymbol{v}}}{2} \right) f_{\text{mass}}^{S,n} \end{pmatrix}, \tag{94}$$

where

$$\begin{aligned} f_{m,i}^{S,n} &= \overline{v}^n \widetilde{\boldsymbol{\rho}}, \\ f_{\text{mass}}^{S,n} &= \sum_{i=1}^{n_c} f_{m,i}^{S,n}, \\ p^* &= \frac{\overline{\rho R_{\text{mix}}}}{\overline{\mathcal{Z}}_T}. \end{aligned} \tag{95}$$

This flux function requires logarithmic averages of the species densities and the temperature, which may be computed affordably with the algorithm presented by Roe and Ismail [16]. The momentum flux involves the total mass flux and a consistent approximation of the pressure as recommended by Chandrashekar [6]. Observe that the total energy flux involves species energies combined through the mass fluxes based on the logarithmic average. We note that in the limit of a single chemical species the flux reduces very nearly to the flux derived by Chandrashekar [6]. Finally, by direct calculation we verify that (94) is indeed a consistent flux, satisfying Equation (13).

5.2.2. *Thermally Perfect Mixtures*

Now we consider a thermally perfect mixture. The $\boldsymbol{g}$ vector is the same as in Equation (93). The H^T matrix has the same form as Equation (91) except for the $\omega_{\text{total},i}$ term. The general result for this term is

$$\omega_{\text{total},i} = \overline{\mathcal{Z}}_T \frac{\Delta e_{\text{total},i}}{\Delta \mathcal{Z}_T} - \frac{\Delta \chi_i}{\Delta \mathcal{Z}_T} + \overline{e}_{\text{total},i}. \tag{96}$$

where

$$\chi_i(T) = \int_{T^\circ}^{T} \frac{c_{v,i}}{T} dT, \tag{97}$$

is the temperature integral in the species entropy. Now the task for a particular heat capacity model is to evaluate $\omega_{\text{total},i}$, which requires the jump ratios of the energy and the entropy temperature integral for each species. We accomplish this in §5.2.3 and §5.2.4, respectively, for the polynomial heat capacity and modal energy models discussed earlier. The resultant flux function takes the form given in (94) and (95).

5.2.3. Thermally Perfect Mixtures: Polynomial Heat Capacities

Here we specialize (94) to NASA-9 polynomials for heat capacities described in §3.3.1. Application of the polynomial forms and tedious algebra shows that each species' contribution to the energy flux in (94) may be computed in the following form, which is a consistent approximation of the species energy in (26).

$$\omega_{\text{total},i} = \frac{R_i}{\widehat{Z_T}} \left(\phi_1 a_{i,1} + \phi_2 a_{i,2} + \phi_3 a_{i,3} + \phi_4 a_{i,4} + \phi_5 a_{i,5} + \phi_6 a_{i,6}\right), \tag{98}$$

$$\begin{aligned}
\widehat{\mathcal{Z}_T} &= -\mathcal{Z}_{T,r}\mathcal{Z}_{T,\ell}, \\
\phi_1 &= \frac{\left(\widetilde{\mathcal{Z}_T} - \overline{\mathcal{Z}_T}\right)\widehat{\mathcal{Z}_T}}{\widetilde{\mathcal{Z}_T}}, \\
\phi_2 &= \frac{\left(4\,\widetilde{\mathcal{Z}_T}\,\overline{\mathcal{Z}_T}^4\,\overline{T}^2\overline{T^2} + \widetilde{\mathcal{Z}_T}\,\overline{\mathcal{Z}_T}^4\,\overline{T^4}\right)\overline{\mathcal{Z}_T} + \left(4\,\widetilde{\mathcal{Z}_T}\,\overline{\mathcal{Z}_T}^2\,\overline{T^5}\,\overline{\mathcal{Z}_T}^{\,2} + 1\right)\widehat{\mathcal{Z}_T}}{\widetilde{\mathcal{Z}_T}}, \\
\phi_3 &= -4\,\overline{\mathcal{Z}_T}^3\,\overline{T}\,\overline{T^2} + \frac{1}{2}\left(4\,\overline{\mathcal{Z}_T}^3\,\overline{T}^2\overline{T^2} + \overline{\mathcal{Z}_T}^3\,\overline{T^4}\right)\overline{\mathcal{Z}_T} + \frac{1}{2}\left(2\,\overline{T^5}\,\overline{\mathcal{Z}_T}^{\,3} + \overline{\mathcal{Z}_T}^2\,\overline{T^5}\,\overline{\mathcal{Z}_T} - 4\,\overline{T^4}\,\overline{\mathcal{Z}_T}^{\,2} - 2\,\overline{\mathcal{Z}_T}^2\,\overline{T^4}\right)\widehat{\mathcal{Z}_T}, \\
\phi_4 &= -2\,\overline{\mathcal{Z}_T}^2\,\overline{T}\,\overline{T^2} + \frac{1}{3}\left(4\,\overline{\mathcal{Z}_T}^2\,\overline{T}^2\overline{T^2} + \overline{\mathcal{Z}_T}^2\,\overline{T^4}\right)\overline{\mathcal{Z}_T} + \frac{1}{3}\left(2\,\overline{T^5}\,\overline{\mathcal{Z}_T}^{\,2} - 3\,\overline{T^4}\,\overline{\mathcal{Z}_T}\right)\widehat{\mathcal{Z}_T}, \\
\phi_5 &= -\frac{4}{3}\,\overline{T}\,\overline{T^2}\,\overline{\mathcal{Z}_T} + \frac{1}{4}\left(4\,\overline{T}^2\overline{T^2} + \overline{T^4}\right)\overline{\mathcal{Z}_T}^{\,2} + \frac{1}{12}\left(3\,\overline{T^5}\,\overline{\mathcal{Z}_T} - 4\,\overline{T^4}\right)\widehat{\mathcal{Z}_T}, \\
\phi_6 &= -\overline{T}\,\overline{T^2} + \frac{1}{5}\left(4\,\overline{T}^2\overline{T^2} + \overline{T^4}\right)\overline{\mathcal{Z}_T}.
\end{aligned} \tag{99}$$

Compared to the flux vector for the calorically perfect case, (94), this flux vector requires only extra addition and multiplication operations. It requires the same number of expensive logarithmic averages which dominate computational cost. We note that, although not performed here, these results can be simplified by expressing averages of the x^n in terms of averages of x.

5.2.4. Thermally Perfect Mixtures: Modal Energy Approach

When the energy is modeled per mode as in §3.3.2, simplification of $\omega_{\text{total},i}$ is complicated by the form of the vibrational energy (29). As energies are additive in (31) the energy and the average and jump operators are linear, $\omega_{\text{total},i}$ can be split into each mode. With only the translational and rotational modes the flux is the same as for the calorically perfect gas in (94). Thus, the flux function is (94) augmented by the vibrational mode's contribution and the $\omega_{\text{total},i}$ term is

$$\omega_{\text{total},i} = \Delta e^{\circ}_{f,1} + \omega_{tr,i} + \omega_{v,i}, \tag{100}$$

$$\omega_{tr,i} = \frac{3 + 2\nu_i}{2} R_i \left(\frac{1}{\widetilde{\mathcal{Z}}_T} - T^{\circ}\right), \tag{101}$$

$$\omega_{v,i} = \overline{e_{v,i}} + \overline{\mathcal{Z}}_T \frac{\Delta e_{v,i}}{\Delta \mathcal{Z}_T} - \frac{\Delta \chi_{v,i}}{\Delta \mathcal{Z}_T}. \tag{102}$$

This shows that extending entropy conservative flux functions to thermally perfect mixtures modeled with the modal energy approach requires simplification of the jump ratios of $e_{v,i}$ and $\chi_{v,i}$, which is nontrivial because these are nonlinear functions of the temperature. Written in terms of $\mathcal{Z}_T = 1/T$ and $\mathfrak{F}_i = \exp(\Theta_i \mathcal{Z}_T) - 1$, these functions are

$$\begin{aligned}
e_{v,i} &= \nu_i R_i \Theta_i \mathfrak{F}_i^{-1}, \\
\chi_{v,i} &= \nu_i \left((\mathfrak{F}_i + 1)\mathcal{Z}_T e_{v,i} - \frac{e^{\Theta_i/T^{\circ}}}{T^{\circ}} e_{v,i}(T^{\circ}) - R_i \ln\left[\frac{\mathfrak{F}_i}{e^{\Theta_i/T^{\circ}} - 1}\right]\right),
\end{aligned} \tag{103}$$

Calculating their jump expansions yields the following flux term, verified to be a consistent approximation of the species vibrational energy,

$$\omega_{v,i} = \nu_i \left(-\overline{\mathfrak{F}}_i \overline{e}_{v,i} + \left[\frac{R_i}{\widetilde{\mathfrak{F}}_i} - \overline{e}_{v,i} \overline{\mathcal{Z}}_T + \left(\overline{\mathcal{Z}}_T - \overline{\mathcal{Z}_T[\mathfrak{F}_i + 1]} \right) \frac{R_i \Theta_i}{\widehat{\mathfrak{F}}_i} \right] \frac{\Delta \mathfrak{F}_i}{\Delta \mathcal{Z}_T} \right). \tag{104}$$

Note the presence of an additional logarithmic average $\widetilde{\mathfrak{F}}_i$ as well as the 'inverse average' $\widehat{\mathfrak{F}}_i = -\mathfrak{F}_{i,\ell}\mathfrak{F}_{i,r}$. To complete the expansion we need to approximate the $\Delta\mathfrak{F}_i/\Delta\mathcal{Z}_T$ term with a Taylor series, analogous to the logarithmic average [16]. The jump ratio of $\mathfrak{F}_i$ reduces to that of an exponential function,

$$\frac{\Delta \mathfrak{F}_i}{\Delta \mathcal{Z}_T} = \frac{\Delta \exp(\Theta_i \mathcal{Z}_T)}{\Delta \mathcal{Z}_T} = \frac{\Delta \exp(\Theta_i \mathcal{Z}_T)}{\Delta(\Theta_i \mathcal{Z}_T)} \frac{\Delta(\Theta_i \mathcal{Z}_T)}{\Delta \mathcal{Z}_T} = \frac{\Theta_i}{[\Theta_i \mathcal{Z}_T]_{\text{exp}}}, \tag{105}$$

wherein we define the new 'exponential average' denoted $[x]_{\text{exp}}$ for any quantity x. This average is defined as

$$[x]_{\text{exp}} = \frac{\Delta x}{\Delta \exp(x)}, \tag{106}$$

and its reciprocal may be computed as in (87) with a Taylor series expansion for small Δx and directly with large Δx. The series expansion is

$$[x]_{\text{exp}}^{-1} = \frac{\Delta \exp(x)}{\Delta x} = \exp(x) \sum_{i=1}^{\infty} \frac{(\Delta x)^{i-1}}{i!}, \tag{107}$$

We find that the first five terms of the series yield machine precision accuracy for $\Delta T \leq 10\,\mathrm{K}$ at temperatures above $3000\,\mathrm{K}$ experienced in shocks in hypersonic flight and flame fronts in combustion. This choice based on comparison of the direct jump calculation and the Taylor series with arbitrary precision floating point in SageMath [24]. With five terms an efficient implementation in Horner form is

$$\frac{\Delta \mathfrak{F}_i}{\Delta \mathcal{Z}_T} = \Theta_i \exp(\Theta_i \mathcal{Z}_T) \left(1 + \delta \left(\frac{1}{2} + \delta \left(\frac{1}{6} + \delta \left(\frac{1}{24} + \delta \frac{1}{120} \right) \right) \right) \right), \tag{108}$$

in which $\delta = \Theta_i \Delta \mathcal{Z}_T$. Adding terms to the series to further improve accuracy for larger ΔT is straightforward, as the numerical coefficients in (108) follow the factorial pattern (*e.g.*, $1/720$ and $1/5040$ follow for a seven-term expansion). Given this affordable implementation of the 'exponential average' the flux term (104) may be evaluated for each diatomic species and so the entropy conservative energy flux may be computed. With the mass and momentum fluxes in (94) we thus have an entropy conservative two-point flux function for thermally perfect mixtures with heat capacities represented as either polynomials (§5.2.3) or with the modal decomposition. Compared to the calorically perfect and polynomial thermally perfect cases, which require $n_c + 1$ logarithmic averages, the flux for the modal approach requires $n_c + 1 + n_{\text{vib}}$ for a mixture of n_{vib} diatomic species, in addition to n_{vib} 'exponential averages' shown in (108).

5.3. Flux Functions for Multitemperature Mixtures

To construct entropy conservative two-point flux functions for multitemperature mixtures we follow the same procedure as in §5.2. Here the parameter vector $\boldsymbol{\mathcal{Z}}$ expands to include each internal mode that is modeled and we explicitly compute internal energy fluxes. We first consider two-temperature (translational-rotational and vibrational-electronic) mixtures in §5.3.1 and then show a three-temperature flux in §5.3.2.

5.3.1. Two-Temperature Mixtures

A convenient choice of the parameter vector is to simply incorporate the inverse of the vibrational temperature as was done earlier for the translational temperature,

$$\boldsymbol{\mathcal{Z}} = \begin{pmatrix} \mathcal{Z}_{\boldsymbol{\rho}} \\ \mathcal{Z}_{\boldsymbol{v}} \\ \mathcal{Z}_T \\ \mathcal{Z}_{T_v} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\rho} \\ \boldsymbol{v} \\ 1/T \\ 1/T_v \end{pmatrix}. \tag{109}$$

This leads to the following H matrix for a two-species, one-dimensional case. The $\boldsymbol{g}$ vector is the same as in (93) with an extra zero appended.

$$\mathrm{H}^{\mathsf{T}} = \begin{bmatrix} R_1/\widetilde{\rho}_1 & 0 & 0 & 0 & 0 \\ 0 & R_2/\widetilde{\rho}_2 & 0 & 0 & 0 \\ -\overline{v}_0\overline{\mathcal{Z}}_T & -\overline{v}_0\overline{\mathcal{Z}}_T & \overline{\mathcal{Z}}_T & 0 & 0 \\ -\frac{\overline{\boldsymbol{v}^{\mathsf{T}}\boldsymbol{v}}}{2} + \Delta e^{\circ}_{f,1} + \omega_{tr,1} & -\frac{\overline{\boldsymbol{v}^{\mathsf{T}}\boldsymbol{v}}}{2} + \Delta e^{\circ}_{f,2} + \omega_{tr,2} & \overline{v}_0 & -1 & 1 \\ \omega_{v,1} & \omega_{v,2} & \overline{v}_0 & 0 & -1 \end{bmatrix}, \tag{110}$$

where $\omega_{tr,i}$ is given in (101) and $\omega_{v,i}$, now a function of T_v, is given in (102). The entropy conservative flux function for this two-temperature mixture is

$$\boldsymbol{f}^{S,n} = \begin{pmatrix} f^{S,n}_{m,i} \\ \overline{\boldsymbol{v}} f_{\text{mass}} + p^{*}\boldsymbol{n} \\ \sum_{i=1}^{n_c} f^{S,n}_{m,i}\left[e^{\circ}_{f,i} + \omega_{tr,i}\right] + p^{*}\overline{v}^{n} + \left(\overline{\boldsymbol{v}}^{\mathsf{T}}\overline{\boldsymbol{v}} - \frac{\overline{\boldsymbol{v}^{\mathsf{T}}\boldsymbol{v}}}{2}\right) f^{S,n}_{\text{mass}} + f^{S,n}_{\text{vib}} \\ f^{S,n}_{\text{vib}} \end{pmatrix}, \tag{111}$$

where (95) applies and the vibrational energy flux is

$$f^{S,n}_{\text{vib}} = \sum_{i=1}^{n_c} f^{S,n}_{m,i}\,\omega_{v,i}. \tag{112}$$

Note that the vibrational flux has the same form as in (104), with the difference being that here it depends upon the vibrational temperature. Thus, simply replacing $\mathcal{Z}_T \rightarrow \mathcal{Z}_{T_v}$ in (104) and (108) yields the jump ratios needed above to compute the vibrational energy flux. This shows that, compared to the thermally perfect (modal energy form) flux derived earlier, no additional cost is incurred due to the extra temperature. Rather we've simply changed the temperature used in evaluating the vibrational energy flux.

5.3.2. Three-Temperature Mixtures

For a three-temperature mixture we use $\mathcal{Z}_{T_r} = 1/T_r$ as for the other temperatures and obtain the energy flux below, following the same procedure as before. Note that this form requires an additional logarithmic average, of the rotational temperature, compared to the prior fluxes.

$$\boldsymbol{f}^{S,n} = \begin{pmatrix} f_{m,i}^{S,n} \\ \overline{\boldsymbol{v}} f_{\text{mass}} + p^* \boldsymbol{n} \\ \sum_{i=1}^{n_c} f_{m,i}^{S,n} \left[e_{f,i}^{\circ} + \omega_{t,i} \right] + p^* \overline{v}^n + \left(\overline{\boldsymbol{v}}^{\mathsf{T}} \overline{\boldsymbol{v}} - \frac{\overline{\boldsymbol{v}^{\mathsf{T}} \boldsymbol{v}}}{2} \right) f_{\text{mass}}^{S,n} + f_{\text{vib}}^{S,n} + + f_{\text{rot}}^{S,n} \\ f_{\text{rot}}^{S,n} \\ f_{\text{vib}}^{S,n} \end{pmatrix}, \tag{113}$$

$$\begin{aligned} \omega_{t,i} &= \frac{3R_i}{2} \left(\frac{1}{\widetilde{\mathcal{Z}}_T} - T^{\circ} \right), \\ \omega_{r,i} &= \nu_i R_i \left(\frac{1}{\widetilde{\mathcal{Z}}_{T_r}} - T^{\circ} \right), \\ f_{\text{rot}}^{S,n} &= \sum_{i=1}^{n_c} f_{m,i}^{S,n} \omega_{r,i}. \end{aligned} \tag{114}$$

6. CONCLUSIONS

Entropy stability has proven to be a useful property in designing numerical methods for compressible flow. To extend classical theory to applications such as combustion and hypersonic flight we have considered the symmetrization and entropy stability of the equations governing multicomponent, multitemperature flows. We have demonstrated entropy stability for such systems based on thermodynamic entropy functions. Stability places strict requirements on models for heat and mass diffusion, which we have explored in detail.

With the continuous stability proof in hand, we've constructed entropy conservative two-point flux functions for simulation in conservation form. This allows a mimetic stability proof for the semi-discrete form when recently developed [9] summation-by-parts operators are employed. The development of entropy conservative flux functions for complex multicomponent, multitemperature systems has motivated a novel automation of the derivation process with symbolic algebra code. Additionally we demonstrate how the use of a newly defined 'exponential average' similar to the logarithmic average of Roe and Ismail [16] allows affordable calculation of flux functions in thermally perfect mixtures. Additional requirements on the discretization for stability at the semi-discrete level are summarized in §5. The advancements presented herein are both an extension of entropy stability to flows that exhibit thermochemical nonequilibrium and generally useful techniques for building entropy stable schemes for other systems.

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